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FORMATION AND REACTIONS OF ALKENE DIIODIDES

BY

HODGE F. MacEWEN

A THESIS

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The undersigned certify that they have read, and recommend
to the Faculty of Graduate Studies for acceptance, a thesis entitled,
FORMATION AND REACTIONS OF ALKENE DIIODIDES
submitted by Hodge F. MacEwen, in partial fulfilment of the requirements
for the degree of Doctor of Philosophy.

ABSTRACT

Cyclohexene-iodine addition is a readily reversible reaction. The extents of cycloalkene diiodide formation upon reaction of an equimolar quantity of iodine with cyclohexene, 4-methylcyclohexene, 3-methylcyclohexene, 4-t-butylcyclohexene, 4,4-dimethylcyclohexene, and cyclopentene, were determined both by n.m.r. spectroscopy and by iodometric analysis. Equilibrium constants (K_{Eq}) were measured at 0.0° and 25.0°, and values for ΔF , ΔH , and ΔS were calculated.

The n.m.r. spectra of the equilibrium reaction solutions indicated trans-addition of iodine. Except in the case of 4,4-dimethylcyclohexene, the cycloalkene trans-diiodides had a strong preference for the conformer wherein both iodine atoms are in axial orientation. The relative values of K_{Eq} were correlated with the relative stabilities of the most favorable conformation available in each case to the product of cycloalkene-iodine addition.

Illumination or degassing of the reaction solution dramatically accelerated the rate of cyclohexene-iodine addition. In the dark in undegassed solvent, the addition reaction proceeded at a rate dependent upon solvent polarity; moreover, in carbon tetrachloride-methylene chloride, the rate of cyclohexene-iodine addition was accelerated by iodide or perchlorate ion.

Iodine in neat cyclohexene (equimolar amounts) underwent a

side reaction to give polymer and cyclohexyl iodide in large amounts. Low temperature and/or dilution with solvent inhibited this reaction.

Iodide, bromide, chloride, acetate, methoxide, or thioethoxide ion readily deiodinated cyclohexene diiodide. In the case of chloride ion and acetate ion, however, extensive secondary reactions occurred and gave rise to cyclohexene trans-chloroiodide and cyclohexene trans-acetoxyiodide, respectively. Under special reaction conditions (no solvent) sodium ethyl mercaptide reacted with cyclohexene diiodide to give 1,2-bis(ethylthio)cyclohexane.

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- (1) The first of these is the fact that the number of cases of the disease has been increasing steadily since 1950. This is due to a number of factors, including a change in the habits of the population, and a general increase in the standard of living.
- (2) The second factor is the fact that the disease is now being found in many more countries than it was in 1950. This is due to the fact that the disease is now being spread by air travel, and by the movement of people from one country to another.
- (3) The third factor is the fact that the disease is now being found in many more people than it was in 1950. This is due to the fact that the disease is now being spread by air travel, and by the movement of people from one country to another.
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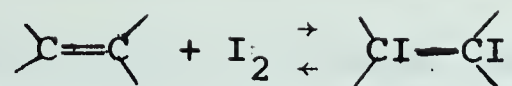
INTRODUCTION

Vicinal diiodides, the products of addition of iodine to alkenes, are compounds seldom encountered in organic chemistry. Besides ethylene diiodide, a colorless, crystalline compound that melts at 82° (1), the only simple, unsubstituted alkene diiodides that have been isolated are those of 1-butene (m.p. -15°)(2), trans-2-butene (m.p. -11° dec.)(2, 3), cis-2-butene (m.p. -24 to -23°)(3), and cyclobutene (m.p. 48°)(4). However, the diiodides of tetrafluoroethylene (b.p. 113°)(5), of styrene (m.p. near 0°)(6), and of allyl alcohol (m.p. 43°)(7) have been obtained.

Several diiodides of strained cyclic or bicyclic alkenes have, also, been characterized. These are the diiodides of aldrin (a substituted bicycloheptene)(m.p. $186-189^{\circ}$)(8), of 9,10-ethenoanthracene (m.p. $146.5-147^{\circ}$)(9), and of benzocyclobutadiene (10, 11). Benzocyclobutadiene appears to be the only cycloalkene for which both a cis-diiodide (m.p. $150.1-150.8^{\circ}$ in the dark, and $146-146.5^{\circ}$ in the light)(10, 11) and a trans-diiodide (m.p. $62-63^{\circ}$)(10, 11) have been found. However, alkyne diiodides are known compounds (12), the simplest being acetylene diiodide, for which both a trans-diiodide (13) and a cis-diiodide (14) are known.

The reaction between iodine and an alkene usually results in the establishment of an equilibrium situation which may be represented by

the following equation (12).



Thus, most isolated alkene diiodides, including ethylene diiodide (1), are metastable compounds which tend to decompose to alkene and iodine (12), the iodine being readily noted due to its intense color. Alkene-iodine addition is, therefore, a conspicuously reversible reaction; however, equilibrium positions have been measured in only a few instances (15-18). Mechanistic aspects of iodine-alkene addition have been examined (2, 3, 6, 9, 15-17, 19-26); however, the difficult isolation of alkene diiodides appears to have largely discouraged investigation of their chemical reactions, aside from the reverse reaction (1-3, 16, 20, 21, 25).

The advent of nuclear magnetic resonance (n.m.r.) spectroscopy offered a new technique for the study of these unusual compounds since, by this means, it appeared likely, especially at high concentrations, that their formation and reactions could be studied in situ in the presence of alkene and iodine. Accordingly, we undertook a study of alkene diiodides, the extent of their formation under equilibrium conditions, the mechanism of their formation, and their general chemical properties.*

*After our work had begun, the use of n.m.r. spectroscopy in determining the extent of reaction in a mixture of iodine and 1-pentene was reported by Sumrell et al (27) and, very recently, Tanner and Brownlee (9) have employed the same tool in a study of the reaction of iodine with 9,10-dihydro-9,10-ethenoanthracene.

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Cyclohexene diiodide, which appeared to be an uncharacterized compound (28, 29), was chosen as a model compound.* Cyclohexene is not only a simple alkene, which is readily available and easily handled, but its diiodide was thought to be of especial interest in view of the conformational properties of the cyclohexane ring. From a comparison of the extent of reaction of iodine with various alkyl-substituted cyclohexenes, we hoped to be able to correlate equilibrium constants with steric effects of the substituents on the cyclohexane ring. As well as determining the equilibrium constants in these reactions and establishing the configuration of the addition products, it was of interest, in the event of trans-addition, the anticipated mode of addition, to determine the positions of equilibrium between the diaxial and diequatorial conformers of the diiodides.

Since bromine and chlorine are halogens similar to iodine, a knowledge of alkene-bromine and alkene-chlorine additions would be expected to be helpful in gaining an understanding of alkene-iodine addition. Accordingly, we have made a survey of alkene-halogen additions.

*After much of our research was completed, an obscure reference (30) to a thesis (16) written about 25 years ago, the results of which, apparently, are otherwise unpublished, was drawn to our attention by Dr. P. J. Dyne, Atomic Energy of Canada, Ltd., Whiteshell Nuclear Research Establishment, Pinawa, Manitoba. This thesis dealt with the reaction of iodine and cyclohexene in benzene; it will be reviewed in the following literature survey.

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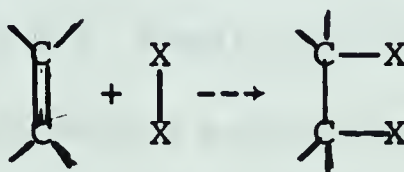
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A BRIEF SURVEY OF HALOGEN-ALKENE ADDITION

General Features of Halogen-Alkene Addition

At the end of the nineteenth century, the process of addition of a halogen molecule to an alkene was regarded as a straightforward, one-step reaction in which the product of addition was assumed to be the cis-adduct (31):



Gradually, however, experimental investigations accumulated evidence showing that the product of addition was often the trans-dihalide rather than the anticipated cis-dihalide (32, 33); hence, the above, four-centered reaction mechanism, at least, as a general reaction mechanism, had to be abandoned. Further investigation, moreover, revealed other complicating factors which frustrated experimental studies and thwarted the erection of any general mechanism for halogen-alkene addition (34-36); these factors, notably, complex kinetics and the occurrence of side reactions, have given rise to much literature that is involved and confusing. This situation has continued to exist almost up to the present day (37, 38).

Two general mechanistic routes are available for halogen-alkene

addition: a heterolytic mechanism, in which ionic or polarized intermediates are involved, and a homolytic mechanism, in which free radical intermediates occur (35-38). The mechanistic path or paths followed in a specific case appear to depend both on the reaction conditions and on the specific reactants (6, 9, 26, 34-43): a medium of high dielectric constant promotes the heterolytic reaction while free radical initiators, including light and heat, promote the homolytic reaction; polar catalysts and free radical inhibitors, e.g., oxygen, may also be influential factors; finally, the stabilities of the specific ionic or free radical intermediates and the ease with which the specific halogens or interhalogens undergo homolysis or heterolysis must be expected to influence the mode of the addition process.

In hydroxylic solvents of high dielectric constant, the reaction that occurs between alkene and halogen is usually a heterolytic, homogeneous process with relatively simple kinetics (37, 43); however, molecules of the hydroxylic solvent may act as nucleophiles and, for example, by attacking carbonium-ion intermediates lead to addition products, other than dihalides (33).

In non-reactive solvents, or in the absence of solvent, other than the alkene, itself, or in the gaseous phase, the only addition products that can arise from reaction between alkene and halogen are vicinal dihalides. The absence of a highly polar medium, however,

frequently allows the occurrence of side reactions and complex kinetics (6, 26, 35-43). Halogen-alkene additions in non-reactive, non-polar solvents, therefore, are complicated reactions, and it is not surprising that these reactions have been variously interpreted as homolytic, homogeneous processes (2, 3, 6, 16, 26, 35-40, 42), as heterolytic, homogeneous processes (6, 9, 17, 26, 34, 39-43), as homolytic, heterogeneous processes (44), and as heterolytic, heterogeneous processes (35-38, 43, 45).

Chlorine-alkene and bromine-alkene additions have, in general, received more attention than fluorine-alkene and iodine-alkene additions (34-36). The great reactivity of fluorine makes its direct addition to alkenes difficult to control and substitution and cleavage reactions occur (46, 47). Recently, however, the addition of elemental fluorine to alkenes has been reported (48).

Although few vicinal diiodides have been characterized* and even ethylene-iodine addition has been dismissed as a reaction that does not readily occur (49), several investigations of iodine-alkene addition have in fact, been undertaken and these will be reviewed.

We should mention, also, that polyhalide ions (50-54) as well as interhalogens (55-58) have been used as agents for addition of halogen to alkenes.

*For a list of vicinal diiodides that have been isolated and characterized, see p. 1.

Scope of Survey

In reviews on the subject of halogen-alkene addition, some authors (35, 36) have discussed both homolytic and heterolytic reactions while others have dealt solely with either ionic reactions (34, 43, 45) or free radical reactions (59-61). Studies of the homolytic process have centered on the photochemical reaction in the gas phase (62); however, Walling (60) has discussed homolytic reactions in solution.

We are concerned primarily with addition of iodine to alkenes; hence, a comprehensive review of halogen-alkene addition would be outside the scope of our research. However, since the bulk of investigation of halogen-alkene additions has been performed with bromine and chlorine, and since anything of fundamental significance in bromine-alkene and chlorine-alkene additions may apply equally well in iodine-alkene additions, it will be necessary to review the important fundamental aspects of the reactions of bromine and of chlorine with simple alkenes. The reaction between halogen and alkene in polar, reactive, hydroxylic solvents has been widely used in mechanistic and kinetic studies aimed at elucidating the initial stages of halogen-alkene addition (33-38); we shall briefly review these investigations but our main concern will be with halogen-alkene additions in inert solvents.

Halogen-Alkene Reaction in Reactive Solvents

The reaction of halogen with alkene in solvents such as water (63), methanol (33), and acetic acid (64) or in the presence of reactive anions (65) leads, in addition to dihalide formation, to the formation of vicinal hydroxy halides, methoxy halides, and acetoxy halides or other vicinal substituted products, depending on the nucleophilic species present. Apparently, these products do not arise from secondary reactions on the dihalides (33); furthermore, in the case of the reaction of stilbene and bromine in methanol, Bartlett and Tarbell (33) concluded that although stilbene methoxy bromide was the principal product of the reaction, methyl hypobromite, arising from the prior reaction of bromine and methanol, was not responsible for its formation. The incorporation of foreign anions and the frequent occurrence of trans-addition (32, 33), led to the proposal that these reactions occurred in two steps, the first step, a rate-controlling step, leading to the formation of a positively charged, reactive intermediate, which could be viewed as arising from the addition of a halogen cation to the alkene (66); such an intermediate would be open to attack by any available nucleophilic species to complete the second step of the addition process; furthermore, trans-addition could be accounted for by attack of the nucleophile on the side of the intermediate opposite to the location of the halogen (33).

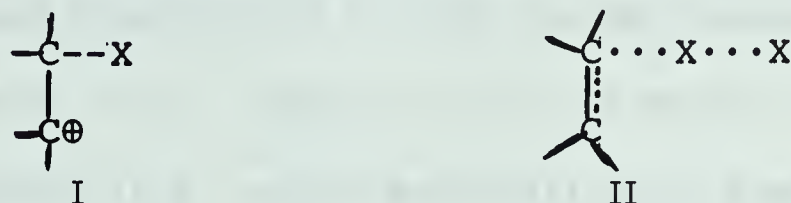
The initial step in the reaction between halogen and alkene involves electrophilic attack of halogen on alkene; this has been shown by a direct

comparison of the rates of reaction of bromine with ethylene and with alkyl-substituted ethylenes in such solvents as methanol (67), water (63), and acetic acid (68, 69), as well as in the inert solvent, methylene chloride (70-72); electron-donating substituents on the ethylenic carbons increase the overall reaction rate. Studies have also shown that the reactivity of X-Y, where at least X is halogen, in an addition reaction with an alkene is increased by increasing the electronegativity of either X or Y (38, 58, 73); if it is X that forms the bond to carbon in the rate-controlling step, then an increase in its electronegativity will increase the strength of the bond; an increase in the electron-withdrawing power of Y will make X even more electrophilic toward the nucleophilic alkene (38).

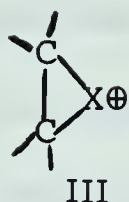
Robertson (45) has shown that in acetic acid solution, the rate of reaction between bromine and simple alkenes changes from a first-order dependence on bromine at a bromine concentration of 0.001 M, to a second-order dependence at a concentration of 0.02 M, and to a third-order dependence at a concentration of 0.2 M. It was thought that as the concentration of halogen increases, more and more molecules of halogen become involved in the rate-controlling step. With bromine at a concentration of 0.02 M, the addition of water was found to cause an increase in the rate and a change from a second-order dependence on bromine to a first-order dependence; on the other hand, addition of

carbon tetrachloride was found to decrease the rate and cause a higher reaction-order dependence on bromine concentration which became about three in pure carbon tetrachloride. In non-polar solvents, it was concluded that heterolysis must be achieved with the aid of several halogen molecules which act to delocalize electrical charge.

Originally, the cationic intermediate was suggested to have the structure of an open carbonium ion (I) (66) which, apparently, was believed to arise from an unsymmetrical transition state (II).



Structure I, as represented, would be a freely rotating carbonium ion and might be expected to give rise to both trans- and cis-products (74). To account for predominant trans-addition in the case of the reaction of bromine with alkenes, Roberts and Kimball (75) pointed out that free rotation about the carbon-carbon bond in the postulated carbonium ion (I) was not to be expected: in this intermediate one of the orbitals of the positively charged carbon must be completely empty while the halogen atom on the other hand has three orbitals occupied by pairs of electrons; this arrangement is such that a coordinate link would be expected to form by the sharing of one of the pairs of electrons of the halogen with the unoccupied orbital of the carbon to give an intermediate of structure III.



However, structure III was not considered to be an entirely accurate picture of the intermediate, rather, the intermediate was considered to be a resonance structure with contributions from both the carbonium ion (I) and the halonium ion (III).

The ionization potential (76) in volts, for the halogens and for carbon are: fluorine, 17.34; chlorine, 12.95; bromine, 11.80; carbon, 11.22; iodine, 10.6; on this basis (75) cyclic bromonium and cyclic iodonium ions would appear to be the halogens most capable of forming halonium ions. The worth of cyclic halonium ions lies in their usefulness in accounting for stereospecific trans-addition: given the configurationally stable intermediate (III), nucleophilic attack may be expected to occur on the side of the molecule opposite to the halogen atom.

Since Roberts and Kimball first proposed the bromonium ion, halonium ions have been invoked to account for stereospecific additions (34 - 38, 43, 50, 64, 69, 77 - 93) and also for solvolytic reactions where a halogen is located on the carbon vicinal to the carbon bonded to the leaving group (94-99). The possibility of chloronium and iodonium ions appear to have first been mentioned by Winstein and Lucas (95). The

first attempt to produce evidence of cyclic chloronium ions was made by Lucas and Gould (96); chloronium ions continue to be postulated (40, 42, 64, 89). Cyclic iodonium ions were invoked by Lucas and Garner (98) to account for the stereochemical changes which occur when concentrated hydrochloric or hydrobromic acid reacts with iodohydrins of known configuration.

de la Mare et al (79-82) postulated the formation of an unsymmetrical intermediate (IV), prior to the formation of III; however Traynham (84, 85) has produced evidence that in the reaction of hypobromous acid



with methylenecyclodecane, a symmetrical bromonium ion is formed and that it is not preceded by an open carbonium ion; however, when chlorine was the entering electrophile, it was concluded that considerable carbonium ion character must be involved in the initial intermediate.

Recently, further data on the relative ease of formation of the various possible halonium ions in methanol was published by Lemieux and Fraser-Reid (93). In the halogenomethoxylations of 2,3-dihydropyran, and of glucal and galactal triacetates, both cis- and trans-additions were observed but the amount of cis-addition decreased on going from chlorine to bromine to iodine; in fact, with iodine no cis-addition was observed.

In these reactions, oxonium-ion formation was considered to be in competition with halonium ion formation; oxonium-ion formation would allow the formation of cis-addition products. Thus, oxonium-ion formation was found to compete favorably with chloronium-ion formation, but poorly with bromonium-ion and even more poorly with iodonium-ion formation.

Halogen-Alkene Addition in Inert Solvents

The reaction of halogens with alkenes in highly polar, inert solvents would be expected to involve a heterolytic mechanism similar to that found in reactive polar solvents but to yield vic-dihalides as the only addition products. In less polar, inert solvents, however, where ionic mechanisms are not facilitated, the product of addition again can only be a dihalide but the pathway or pathways via which the product forms would be expected to be more complex; indeed, this is found to be the case (37). The complex kinetics found experimentally when halogen-alkene addition occurs in inert, non-polar solvents has been attributed not only to the involvement of several molecules of halogen in the rate-determining step of a heterolytic addition process (37, 45) but also to the occurrence of a competing homolytic addition process (6, 26, 39-42), which in the case of alkene-chlorine addition (39-42) is accompanied by free radical substitution processes.

About 30 years ago, Sherman et al (100, 101) calculated the activation energies (ΔH^\ddagger) for ethylene-halogen addition reactions as well as for the reverse reactions (ΔH_r^\ddagger) both for a homolytic mechanism and for a proposed molecular concerted mechanism; the heats of reaction (ΔH) for the forward reactions were also calculated; these values are tabulated below in Table I.

TABLE I

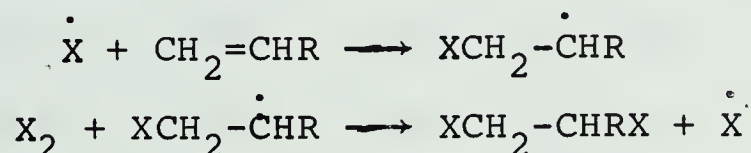
Theoretical activation energies, ΔH^\ddagger , and heats of reaction, ΔH , for halogen-ethylene addition and activation energies, ΔH_r^\ddagger , for dehalogenation of ethylene vic-dihalides (100, 101)

Halogen	ΔH , kcal/mole	ΔH^\ddagger , kcal/mole		ΔH_r^\ddagger , kcal/mole	
		Homolytic Mechanism	Concerted Mechanism	Homolytic Mechanism	Concerted Mechanism
Cl ₂	-55.2	28.5	25.2	78.6 or 57.0	80.4
Br ₂	-25.8	22.6	24.8	43.1 or 37.7	50.2
I ₂	- 7.6	20.5	22.4	27.8 or 28.1	30.0

The calculations of Sherman et al were applicable to reactions in the gas phase or to reactions in inert solvents which do not affect the rate of reaction; the absence of possible catalysts and inhibitors was also a stipulation. Under such reaction conditions it was calculated that for

chlorine, the proposed concerted mechanism of addition was preferable to the proposed homolytic mechanism while for bromine and for iodine the proposed homolytic mechanism was more favorable than the proposed concerted mechanism. However, the differences in the calculated activation energies for the two processes were so small that it was concluded that halogen-alkene addition might operate simultaneously by both processes.

More recently, the energetics of the free radical addition of halogens to alkenes has been examined by Walling (60) in terms of an addition step followed by a displacement step:



To maintain a significant chain length, it was pointed out that both these steps must be very fast in comparison to all chain termination steps; this would require the activation energy for each of the two steps to be small, less than 15 kcal/mole, which is much smaller than the energy required to dissociate the chemical bonds involved; furthermore, the heat of activation, which is a positive quantity, must be greater than or at least equal to the heat of reaction for the respective reaction step.

The heats of reaction, ΔH_A , and ΔH_D , for the above addition step and displacement step, respectively, were estimated by Walling as the differences between the energies of bonds broken and formed in the

individual chain steps; some of these calculated values are listed in Table II.

TABLE II

Calculated heats of reaction in addition step (ΔH_A) and in displacement step (ΔH_D) for halogen-alkene addition via a homolytic chain mechanism at 25° (60)

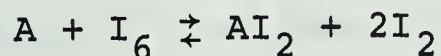
Halogen	ΔH_A kcal/mole			ΔH_D kcal/mole		
	Ethylene	Propene	Styrene	Ethylene	Propene	Styrene
Cl_2	-26	-30	-49	-19	-15	-6
Br_2	- 5	- 9	-28	-17	-13	0
I_2	+ 7	+3	-16	-13	-10	+1

The estimated heats of reaction for the addition of bromine or chlorine to ethylene, propene, or styrene indicate that neither of the reaction steps is likely to be endothermic; in the case of iodine addition, however, although the overall reaction was calculated to be exothermic, one or other of the reaction steps was calculated to be endothermic. Walling concluded that radical addition of iodine to alkenes is at best a marginal proposition.

It seems that halogen-alkene addition must not be assumed, without

compelling evidence, to proceed exclusively by any one pathway. Although it may be generally stated that heterolytic reactions are more favorable in polar solvents and that homolytic processes may be often promoted by free radical initiators or light, or retarded by free radical inhibitors, it should be recognized that under reaction conditions where neither process is especially promoted nor inhibited that it is hazardous to exclude the possible occurrence either of simultaneous or successive homolytic and heterolytic processes.

Iodine-alkene addition in inert, non-polar solvents has been investigated by Bhattacharyya et al (15, 22) and by Robertson et al (17). Bhattacharyya et al (22) studied the addition, in the dark at 0° and 30°, of iodine to 2-pentene and to α -pinene in benzene, carbon tetrachloride, and carbon disulfide, with reactant concentrations in the range of 0.02 to 0.20 M. The rate of the forward reaction was found to be proportional to the first power of the alkene concentration and to the third power of the iodine concentration in agreement with an earlier suggestion by Groh et al (19) that in non-polar solvents hexatomic iodine molecules are responsible for thermal iodination:

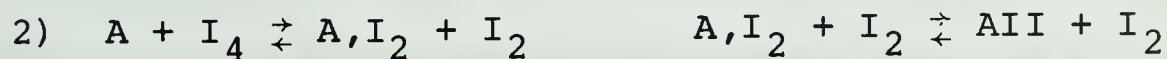


The rate of reaction was found to be solvent dependent, being greatest in benzene and least in carbon disulfide. Bhattacharyya et al used about equimolar quantities of reactants. Robertson et al (17), however,

employed a large excess of alkene in order to reduce the effect of the reverse reaction and the initial rate of the forward reaction at different initial concentrations was measured. Both groups of workers determined iodine concentrations by titrations with standard solutions of sodium thiosulfate. Robertson et al proposed the rate equation:

$$-d(I_2)/dt = k(I_2)^3(A) + k'(I_2)^2(A).$$

In this rate equation, the first term was believed to be the one chiefly operative in solvents such as chlorobenzene, carbon tetrachloride, and carbon disulfide (solvents, all of which gave violet solutions of iodine); the second term was thought to be the important one in solvents such as isobutyl ether, acetic acid, and nitrobenzene (solvents, all of which gave brown solutions of iodine). Robertson et al postulated two alternative schemes available for such fourth-order kinetics,



In either case, the final reaction step was thought to be the relatively slow, rate-determining step.

Neither Robertson et al (17) nor Bhattacharyya et al (15, 22) appear to have considered the possibility that these dark reactions could, in part at least, be homolytic; the effect of oxygen, dissolved in the solvents, was not investigated. In the case of 2-pentene and α -pinene,

Bhattacharyya et al (15) found that the equilibrium constants diminished with increase in temperature and calculations indicated the reaction to be exothermic by four or five kilocalories per mole. Robertson et al (17) attempted to determine equilibrium constants in a number of iodine-alkene additions; however, the solvent employed was acetic acid and since product analysis was not made such measurements may not be very meaningful.

Recently, Sumrell et al (27) noted by means of n.m.r. spectroscopy that when 1.0 mole of pentene and 0.5 mole of iodine were stirred together for a few minutes the ratio of alkene to alkene diiodide was 1:1 and only a small amount of iodine appeared to remain.

No comprehensive, thorough investigation of the mechanism of bromine-alkene addition in non-polar, inert solvents has been performed which is capable of explaining all the involved and complex findings concerned with this reaction. Studies of this reaction have been plagued by the occurrence of heterogeneous reactions and catalysis by water and hydrogen halides (37-39). In the light of the recent investigations with chlorine and iodine, spontaneous homolytic bromine-alkene additions would appear to be another possible complicating factor.

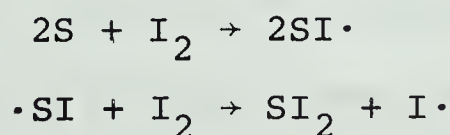
Spontaneous Homolytic Halogen-Alkene Additions

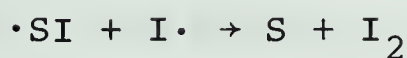
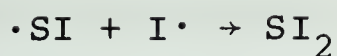
Usually, an initiator is required to start off a free radical process

and to maintain it until the process is complete. Recently, however, spontaneous generation of homolytic processes (102) has been demonstrated to occur. Thus, under conditions that, formerly, were thought to preclude homolytic processes, halogen-alkene addition may proceed via competing homolytic and heterolytic mechanisms.

Bartlett et al have examined the kinetics and mechanism of the formation of styrene diiodide from iodine and excess styrene in carbon tetrachloride at 25°. The uninhibited equilibrium reaction was found to have a half-time of less than two minutes; oxygen and 2,2-diphenyl-1-picrylhydrazyl reduced the rate one-hundred fold; in the presence of the latter inhibitor iodine still disappeared fifteen times as fast as the inhibitor. Hence, the existence of both a radical chain reaction which could be inhibited and a non-radical reaction which could not be inhibited was indicated.

The kinetics of the uninhibited radical reaction, followed by a recording spectrophotometer, showed an overall first-order dependence of the rate on the concentration of iodine and a 3/2-order dependence on the concentration of styrene. Bartlett et al pointed out that these results are consistent with a chain mechanism in which an iodine and two styrene (s) molecules are involved in the initiation of the chain reaction:

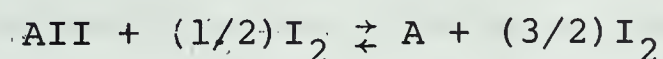




About thirty years prior to the publication of the above work, Polissar (20) had studied the thermal decomposition of ethylene diiodide in carbon tetrachloride at 120-150°; Polissar found that the decomposition was catalyzed by iodine and took place according to the equation:

$$-d(\text{AII})/dt = k(\text{AII})(\text{I}_2)^{1/2}$$

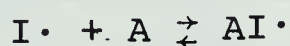
where AII represents the alkene diiodide; this led to the portrayal of the reversible reaction as:



where A represents the alkene; the rate equation for the forward reaction in the synthesis of the diiodide was then represented as:

$$d(\text{AII})/dt = k'(\text{A})(\text{I}_2)^{3/2}.$$

After examining the results of Polissar, Schumacher (21) proposed the following mechanism for the formation and decomposition of ethylene diiodide.



In an otherwise unpublished work, Birkenhauer (16), in a thesis written about 25 years ago, examined the reaction of cyclohexene and iodine in benzene. The rate of reaction was accelerated by illumination

and the reaction was found to be reversible; the position of equilibrium appeared to be independent of light intensity and, therefore, Birkenhauer concluded that both the forward and reverse reactions were light-catalyzed and that the reaction could be described by Schumacher's rate expression:

$$d(\text{AII})/dt = k_1 (\text{A}) (\text{I}_2)^{3/2} - k_2 (\text{AII}) (\text{I}_2)^{1/2}$$

This rate expression was integrated for the case where the initial concentrations of alkene and iodine in the forward reaction were equal. Reactions were carried out in the dark with initial reactant concentrations near 0.025 M; iodine concentrations were determined colorimetrically. The data obtained were found to fit the integrated equation. The values found by Birkenhauer for the specific rate constant, k_1 , and the average equilibrium constants at each of the temperatures employed are given below in Table III. The heat of reaction for the addition reaction was found to be -7.86 kcal/mole.

TABLE III

Rate and equilibrium constants at various temperatures for iodine-cyclohexene addition in benzene, according to Birkenhauer (16).
Each reactant, initially, about 0.025 M

Temperature deg	k_1 (mole/liter) ^{5/2} (h) ⁻¹	K_{Eq} (mole/liter) ⁻¹
5.4	1.84, 2.15	54.5
25.0	2.30, 2.52	20.0
35.0	2.51, 2.67	13.0 [#]

[#]For the reverse run at 35°, the value for K_{Eq} found was 13.3

The mechanism of chlorine-alkene addition has been thoroughly investigated very recently by Poutsma (39-42). Dark chlorination of neat cyclohexene at 25° in the absence of inhibitors and initiators was found to be a free radical process which arose because of spontaneous initiation of radical chains by interaction between chlorine and alkene (39). The radical pathway, however, was found to be superseded by a different process, presumed to be proceeding through ionic intermediates, when radical inhibitors such as oxygen were added or when a polar solvent was used. Even in the absence of inhibitors, Poutsma found the ionic route to begin to compete effectively with the radical process if the alkene was progressively diluted with inert, non-polar solvents.

From a study of some 18 different alkenes (40), Poutsma concludes that dark chlorination of any neat alkene, free from other functionality and in the absence of inhibitors, will lead to a significant fraction of radical reaction except for those alkenes which bear two alkyl groups (or apparently one phenyl group)* on at least one end of the double bond. Previous attempts to correlate chlorination products with alkene structure, therefore, were shown to be inadequate because of the failure to realize the duality of mechanism involved.

A tentative mechanism for alkene-chlorine reaction is proposed

*This was based on the chlorination of styrene which was found to be ionic under all conditions where no external initiation was supplied.

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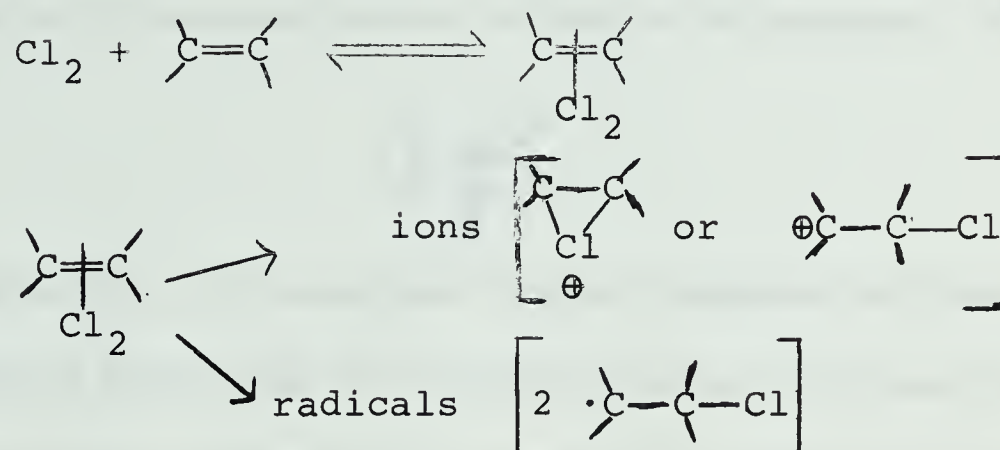
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by Poutsma (40); chlorine could form a pi-complex with the alkene which would be an energy minimum; the complex could then either rearrange to ionic intermediates or react with more alkene to produce radicals. This mechanistic possibility is depicted in the following scheme.



The merits of this scheme, according to Poutsma, are (1) it provides a two-step path for the radical initiation reaction which apparently must be at least a three-body reaction, and (2) it involves a connection between the two pathways, both of which seem to be favored by electron-rich double bonds.

Nature of Intermediate in Inert Non-Polar Solvents

In inert non-polar solvents the mechanism of heterolytic halogen-alkene addition is usually postulated to involve halonium ion (41, 42, 86-88, 90) or an intermediate with characteristics of both carbonium and halonium ions (41, 42, 69, 83), as originally proposed by Roberts and Kimball (75) in the reaction of bromine with alkene in reactive polar

solvents. Cyclic halonium-ion formation, however, is discounted by Dewar (103-106); he prefers to view the intermediate as a pi-complex in which the filled pi-orbital of the alkene is used to form a dative bond by interaction with the empty valence orbital of the acceptor, X^{\oplus} , to give:



If X^{\oplus} has unshared p- or d-electrons, Dewar suggests that these could be used to form a reverse dative bond to the alkene by interaction of the empty anti-bonding pi-molecular orbital of the latter; X^{\oplus} would then be attached to the alkene by a double bond composed of two dative bonds involving pi-molecular orbitals (106). According to Dewar (106) such a structure would differ from the triangular halonium ion only in the state of hybridization of the alkenic carbon bonds since the bond between the two carbon atoms would only be partly double.

Whether or not the intermediate that would be formed between X^{\oplus} and an alkene should be described as a halonium ion or as a pi-complex seems almost a matter of semantics. If the initial electrophilic attack on the alkene is by I^{\oplus} or Br^{\oplus} , the formulation of either a cyclic halonium-ion or a pi-complex would adequately account for the trans-addition obtained. In any case, it seems unreasonable to expect the formation of X^{\oplus} , a charged species in inert solvents. In the ionic addition of hydrogen halides to alkenes, or in the ionic addition of chlorine to alkenes, in each

case of which considerable cis-addition occurs (107-112), an intermediate different from a cyclic halonium-ion or a pi-complex must be formulated; here, Dewar favors a classical carbonium ion or an ion pair.

Dewar postulates that the pi-complex would be more favored the weaker the bond C-X and the less electronegative the moiety X; furthermore, pi-electrons or unshared p- or d-electrons on X would selectively stabilize the pi-complex by back-coordination; also, the carbonium ion might be selectively stabilized by electron-donating substituents on the alkene since they would have a much smaller effect on the stability of the pi-complex. Dewar concludes that, in the case of chlorine, there is an easily upset balance between the two possible intermediates which thereby accounts for the occurrence of both cis- and trans-addition in the chlorine-alkene addition reaction. In hydrogen halide addition via ionic mechanisms, Dewar produces evidence that it occurs via an undissociated ion pair which leads mostly but not exclusively to cis-adducts; it was further postulated that the more polar the solvent, the more likely the intermediate carbonium ion would have an opportunity to lose its stereochemistry, and thereby give rise to trans-adducts.

Speculation on the nature of the intermediates involved in homolytic halogen-alkene additions has been based, in part, on studies of the homolytic addition to alkenes of substances other than halogens, notably hydrogen bromide (113-119) and, in part, on the results of homolytic

January 10, 1912. Dear Sir,

I have the pleasure to acknowledge the receipt of your letter of the 8th inst.

in relation to the matter of the proposed extension of the

term of the lease of the land owned by the State of New York.

I have also the pleasure to inform you that the same has been

referred to the Board of Land Officers for their consideration.

Very respectfully,
J. B. Thompson, Secretary.

Enclosed for you are two copies of the report of the Board of

Land Officers, dated January 8, 1912, in relation to the proposed

extension of the term of the lease of the land owned by the State of

New York, and also a copy of the report of the Board of Land Officers

dated January 8, 1912, in relation to the proposed extension of the

term of the lease of the land owned by the State of New York.

I am, Sir, very respectfully,
Very truly yours,
J. B. Thompson, Secretary.

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Land Officers, dated January 8, 1912, in relation to the proposed

halogenation of alkyl halides (120-122). To account for stereospecific reactions involving bromine and iodine radical reactions, bridged or cyclic alkene-halogen radical intermediates similar to cyclic halonium-ion intermediates have been postulated (3, 116-123); considerable scepticism concerning such intermediates has been raised (116) and, very recently, Haag and Heiba (124, 125) conclude that these stereospecific reactions must be accounted for in terms of short-lived, non-planar, non-bridged intermediates.

Photochemical Alkene-Iodine Addition

The photochemical addition of iodine to alkenes has received investigation by a number of workers. Bhattacharyya (15) found that whereas the reaction of iodine with 2-pentene, for an appreciably fast reaction in the dark, required an iodine concentration greater than 0.02 M, in the presence of light, the reaction proceeded rapidly even at concentrations less than 0.02 M. The rate of addition appeared to be proportional to the concentration of alkene, the concentration of iodine, and to the square root of the intensity of the absorbed radiation (24).

Forbes and Nelson (2, 126), nearly thirty years ago, showed that the addition of iodine to 1-butene at -60 to -90° (reactants each 0.01 M in solution in methylene chloride or chloroform) had proceeded to an extent of 90% or greater after the solution had been illuminated by an incandescent

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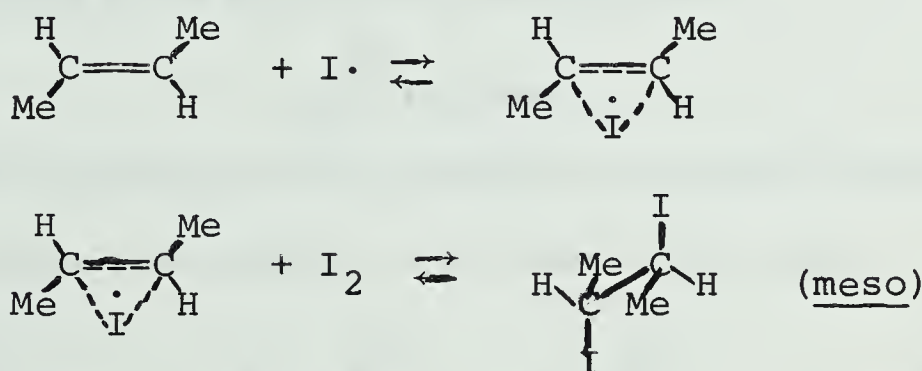
lamp for 3 hours. Subjected to illumination from a spark between high-tungsten steel electrodes for an hour, titration with a solution of sodium thiosulfate showed the butene diiodide had quantitatively eliminated its iodine; another sample, kept at 20° for 100 hours evolved 84% of its iodine. Forbes and Nelson found also, that irradiation at -150° with a tungsten lamp of a solution of iodine and excess butene in dichlorodifluoromethane caused the iodine to disappear; however, it quickly reappeared upon exposure to a spark between tungsten steel electrodes. In chloroform at -55° , the four butenes, propylene, and ethylene were quantitatively photoiodinated in light of wavelengths $436\text{m}\mu$, $546\text{m}\mu$, and in two cases $644\text{m}\mu$; quantum yields appeared to fall off with increasing wavelength; the rate of photoiodination seemed to vary directly with reactant concentrations and light intensity.

Essentially, the above work has been repeated recently by Skell and Pavlis (3); the reaction of iodine (0.1 M) with each of the four butenes (about 4.0 M) at -42° in refluxing propane under illumination from a tungsten filament lamp, was found to give within one-half hour a colorless solution of diiodide. The isolated colorless crystalline compounds were found to decompose to starting materials in yields of 90%. N.m.r. spectra were said to indicate trans-addition and dehalogenation of the 2,3-diiodobutanes with zinc dust in methanol at -78° regenerated the alkene from which the alkene diiodide had been prepared. Skell and Pavlis

proposed a radical chain mechanism:



They claim to have found the order of bridge stabilities to increase in the series $F < Cl < Br$ and hence, they suggest that the most effective bridging halogen in β -haloalkyl radicals should be iodine, just as in halonium ions (3). The stereospecific trans-photoaddition of iodine to alkenes was thus rationalized by Skell and Pavlis by assigning bridge structures to the radical intermediates:



In the work by Trifan and Bartlett on the addition of iodine to styrene (6), it was found that if dilute solutions of iodine, 0.001 M, in styrene which had been equilibrated in the dark were suddenly illuminated with light of wavelength, 500 mμ, increases in the transmission of light of the order of 1% were consistently observed in the spectrometer. Interruption of the light restored initial iodine concentrations and the cycle could be repeated at intervals of about 20 seconds. Contrary to the conclusion of Birkenhauer (16) in the case of iodine and cyclohexene,

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CHICAGO, ILLINOIS 60637

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$$\frac{1}{2} \text{H}_2\text{O} = \text{H} + \frac{1}{2} \text{O}_2$$
$$\text{H}_2\text{O} = \text{H}_2 + \frac{1}{2} \text{O}_2$$

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the results of Trifan and Bartlett indicate the existence of a photo-stationary equilibrium slightly different from the position of equilibrium in the absence of illumination.

Iodine-Catalyzed Isomerizations of Alkenes

Iodine is well known as an effective catalyst for cis-trans isomerization of alkenes (127-135); at high temperatures catalytic amounts of iodine also effect rapid positional as well as geometrical isomerization of alkenes (128-134). The rate of geometrical isomerization generally has been found (133) to be proportional to:

$$(I_2)^{1/2} (\text{Alkene}) ;$$

the appearance of the half-order dependence is usually interpreted as involving an iodine atom addition to the alkene (133, 135):



The iodine atoms can be generated either thermally (129-135) or photochemically (127, 128). The rate-determining step for this mechanism may be either the rate of internal rotation of the two groups in the radical or else the actual addition of the iodine atom to the alkene (133). Benson et al (133) found from their kinetic studies of the iodine-catalyzed isomerizations of butene-2 in the gas phase over the temperature range

137 to 246° that the rate-determining step was the rate of rotation about the single bond. However, Back and Cvetanovic (127) from their study of the cis-trans isomerization of butene-2 at 65° by photochemically generated iodine atoms, conclude that isomerization does not occur entirely by the above mechanism; they consider, in addition, a mechanism involving initial formation of pi-complexes between iodine atoms and butene-2.

Summary

This survey of the literature on halogen-alkene addition has covered mainly those investigations concerning mechanisms of additions of halogens to simple alkenes, especially, in non-reactive, non-polar solvents, iodine-alkene additions being more comprehensively reviewed than alkene-bromine or alkene-chlorine additions.

In inert, non-polar solvents, chlorine-alkene addition has been more thoroughly elucidated than bromine-alkene or iodine-alkene addition. In the absence of free radical inhibitors, this reaction occurs via competing homolytic and heterolytic pathways (39-42). A similar situation has not been demonstrated for bromine-alkene addition; however, Bartlett (6, 26) has concluded that the addition of iodine to styrene in carbon tetrachloride proceeds both by a radical-chain mechanism which can be inhibited by efficient radical-capturing reagents and by a non-radical mechanism which cannot be so inhibited.

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DISCUSSION OF RESULTS

Introduction

This research consists of a study of alkene-iodine addition and reactions of alkene diiodides. The addition reaction was found to be incomplete and readily reversible; using cyclohexene as a model alkene, we have investigated the effects of various factors on the position of equilibrium and on the reaction rate. The most facile reaction of cyclohexene diiodide with nucleophiles was found to be deiodination; however, in some cases, secondary reactions occurred giving rise to β -substituted iodocyclohexanes.

Cyclohexene Diiodide Formation

Cyclohexene and iodine, in equimolar quantities (2.0 M) in carbon tetrachloride were soon found to react readily under ambient laboratory conditions to form cyclohexene diiodide in nearly 85% yield. This information was obtained from a comparison of the n.m.r. spectrum of the reaction solution (Fig. 1) with that of cyclohexene (Fig. 2). The former spectrum, in addition to a signal at τ 4.38 for the ethylenic

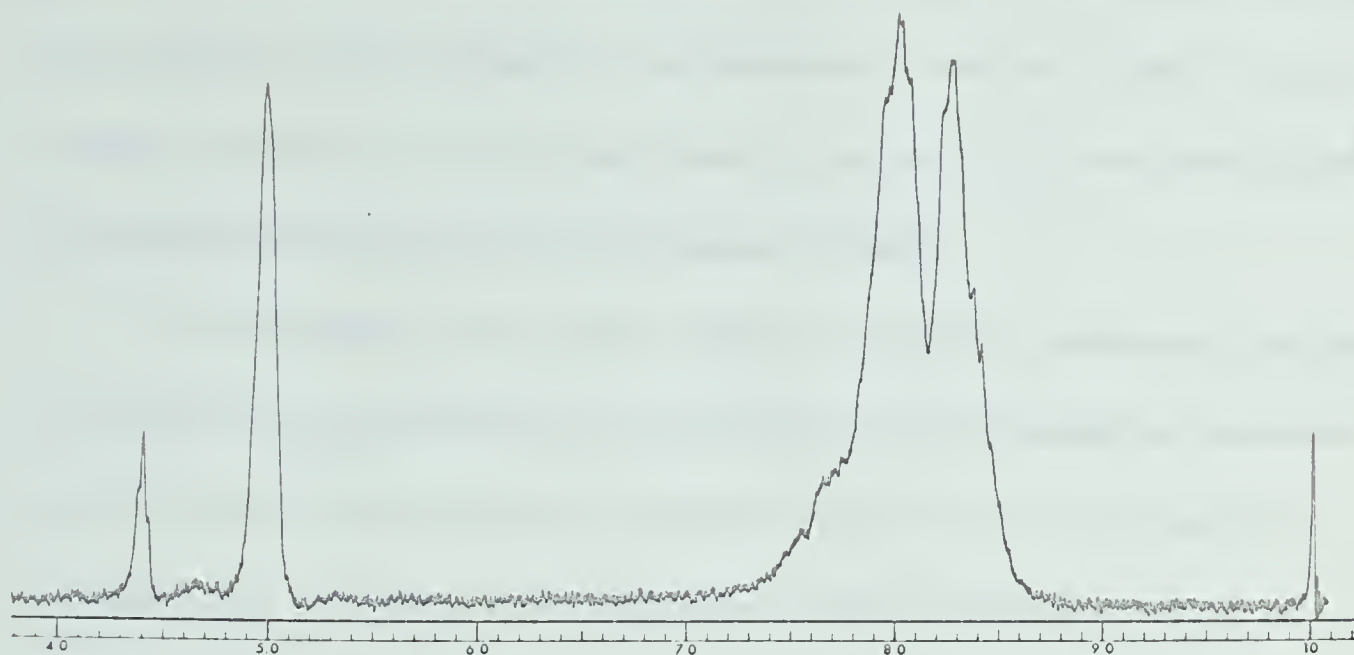


FIG. 1. N.m.r. spectrum (60 Mc.p.s.) of cyclohexene-iodine-cyclohexene diiodide equilibrium mixture in carbon tetrachloride. Cyclohexene and iodine, initially, 2.0 M. Extent of formation of cyclohexene diiodide, 85%.

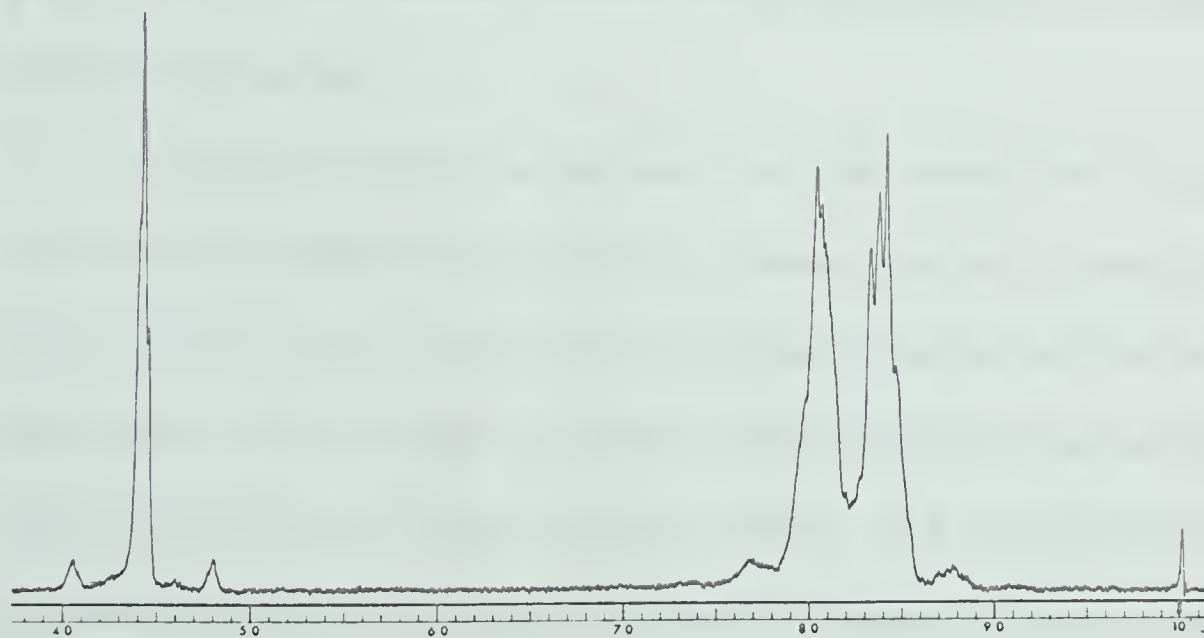
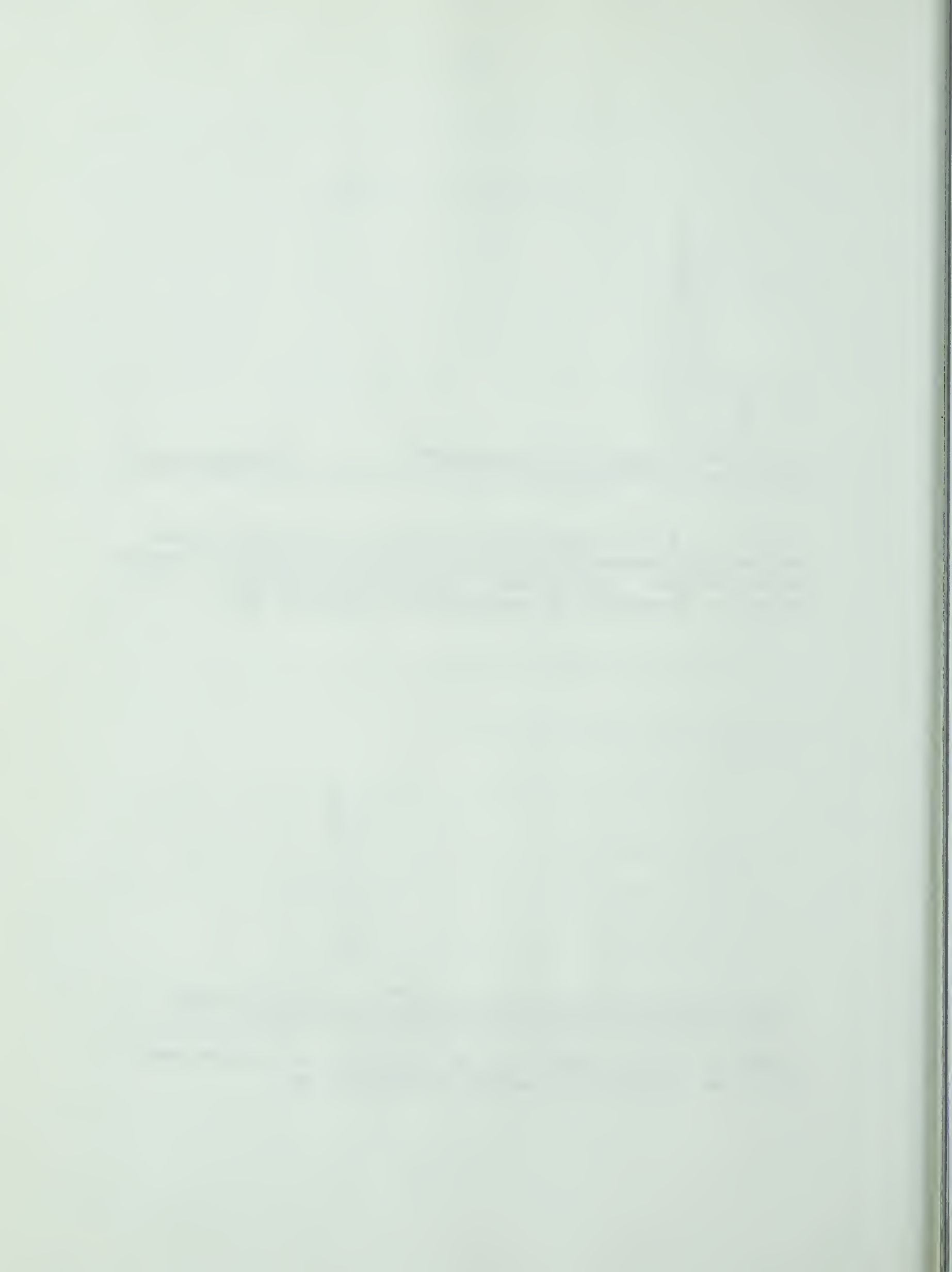


FIG. 2. N.m.r. spectrum (60 Mc.p.s.) of cyclohexene, 50% (v/v) solution in carbon tetrachloride.



protons of cyclohexene (136), showed a signal at τ 4.95, five times the intensity of the signal for cyclohexene; this new signal, in the region expected for protons geminal to iodine (137), was attributed to the methine protons of cyclohexene diiodide.

Illumination with visible light was found to decrease the time required for the attainment of equilibrium in this addition reaction, and the equilibrium constant was perceived to vary inversely with temperature. Thus, by illumination of the reaction solution at temperatures below room temperature, we were able to obtain the diiodide rapidly and in amounts in excess of the equilibrium quantities at room temperature. On allowing such a cooled reaction solution to warm to room temperature under illumination, it was found that the same equilibrium position as that attained in the forward reaction was rapidly approached.

For concentrated solutions in carbon tetrachloride these observations were made directly by means of n.m.r. spectroscopy. It was found, also, that the concentration of unreacted iodine could be measured with precision by rapidly shaking or stirring an aliquot of the reaction mixture with an excess amount of a standardized, aqueous solution of sodium thiosulfate and back titrating the excess sodium thiosulfate in the aqueous phase with a standardized, aqueous solution of iodine. For dilute solutions, this technique of iodometric analysis

proved invaluable.

The addition of iodine to cyclohexene was confirmed by means of ultraviolet and visible spectroscopy. For dilute solutions of reactants in carbon tetrachloride, it was observed that as the absorption band due to iodine, near $520\text{ m}\mu$, decreased during the forward reaction, a new absorption band appeared and increased in intensity in that region of the ultraviolet, near $275\text{ m}\mu$, where the carbon-iodine bond is known to absorb (138-140). Iodine-free solutions of cyclohexene diiodide in carbon tetrachloride could be obtained by briefly, but vigorously, shaking the carbon tetrachloride reaction solution with an aqueous solution of sodium thiosulfate and separation of the organic phase. However, iodine-free solutions of cyclohexene diiodide were found to eliminate iodine; as this process proceeded and the band in the visible region due to iodine grew in intensity, the band near $275\text{ m}\mu$ in the ultraviolet region gradually decreased in intensity. Both the forward and reverse reactions proceeded much more rapidly in the light than in the dark.

In spite of its instability, we found, by working rapidly in dim light, that it was possible to isolate virtually pure cyclohexene diiodide from its reaction solution in carbon tetrachloride. Removal of unreacted iodine from the reaction solution with an aqueous solution of sodium thiosulfate, followed by separation, drying, and evaporation under reduced pressure of the resulting colorless organic layer, gave a faintly

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yellow syrup which, with further pumping off of the solvent under high vacuum at low temperature, gave a white crystalline product which melted at about -5° .

The n.m.r. spectrum of this substance, in neat form shown in Fig. 3, corresponds to that expected for cyclohexene diiodide, and is similar to that for cyclohexene dibromide (Fig. 4). Integration showed the relative intensities of the signal at τ 4.95 and of the signals at higher field (due to methylenic hydrogens) to be 1 : 4.2 (expected for cyclohexene diiodide, 1:4). Initially, there was no evidence in the n.m.r. spectrum for cyclohexene; however, upon standing either in the dark or the light, samples of the neat diiodide underwent deiodination, (iodine formation was visibly detected) and a signal in the n.m.r. spectrum at τ 4.38 appeared and approached an equilibrium intensity, corresponding to 10-15% deiodination of the diiodide.

Formation of Cyclohexyl Iodide — a Side Reaction in Cyclohexene-Iodine Addition

At 25° , the addition of crystalline iodine to neat cyclohexene was found to result in a strongly exothermic process in which more than one mole of iodine could be dissolved in one mole of cyclohexene to give a dark brown solution. On standing, such solutions became more viscous, deposited a black polymer, gave off acidic fumes (presumably,

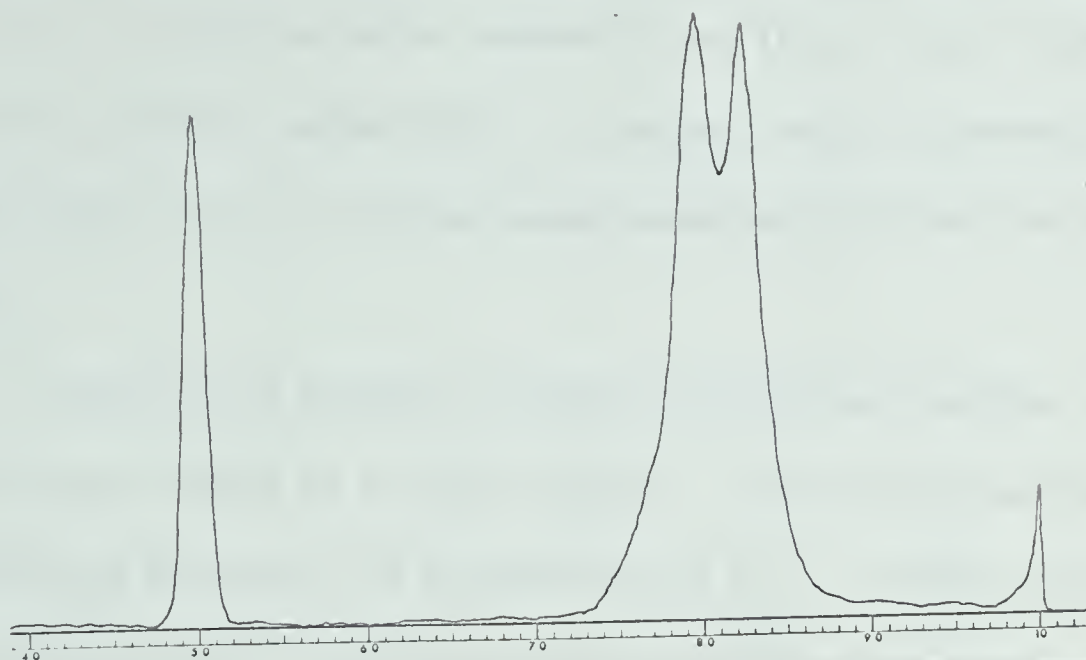


FIG. 3. N.m.r. spectrum (60 Mc.p.s.) of freshly prepared, neat cyclohexene diiodide.

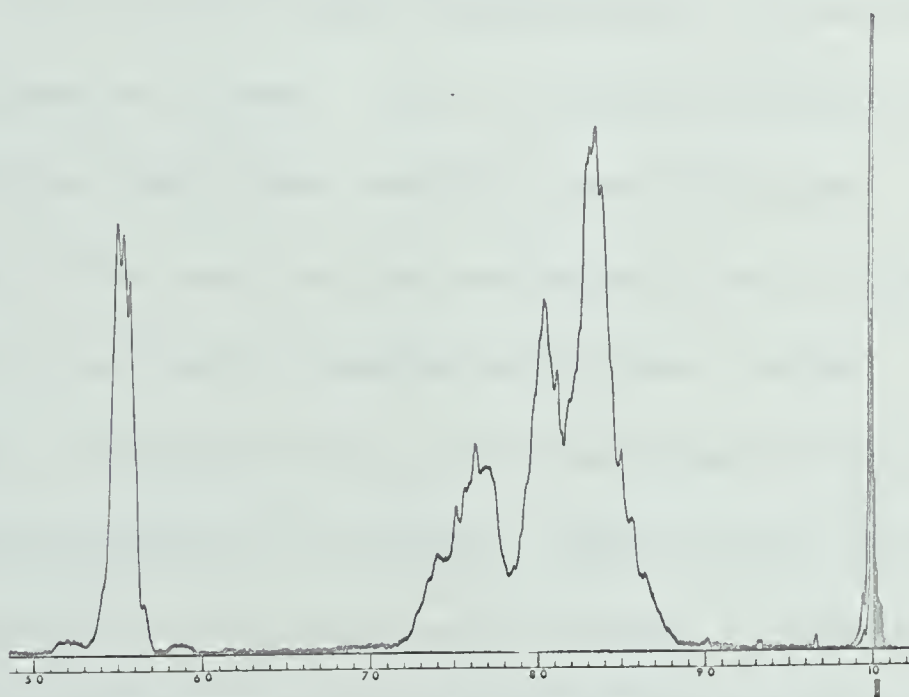


FIG. 4. N.m.r. spectrum (60 Mc.p.s.) of cyclohexene trans-dibromide.

hydrogen iodide), and produced cyclohexyl iodide in large amounts. The n.m.r. spectrum of the mother liquor (Fig. 5) was identical with that for cyclohexyl iodide (Fig. 6), having a septet centered at τ 5.5 (half-width, 17 c.p.s.) in the region expected (141) for the methine proton.

Pyrolysis of freshly prepared cyclohexene diiodide, also, led to cyclohexyl iodide as a major product. Thus, when samples of cyclohexene diiodide were injected onto a g.l.c. column at an inlet temperature of 240° , cyclohexyl iodide could be collected at the column outlet.

Recently, Dvorko and Shilov (142) have claimed that the addition of hydrogen iodide to cyclohexene in benzene requires iodine as a catalyst; further, they propose that hydrogen iodide-cyclohexene addition proceeds via cyclohexene diiodide. Also, recently, Eberhardt (143) has reported that hydrogen iodide adds readily to neat cyclohexene; apparently, the hydrogen iodide used here was not entirely free of iodine, so that iodine may have been a catalyst in this case, as well. Therefore, in our case, cyclohexyl iodide could have arisen from hydrogen iodide-cyclohexene addition, the hydrogen iodide, in turn, having arisen from a dehydroiodination of cyclohexene diiodide, brought about by traces of iodide ion (triiodide ion, in the presence of excess molecular iodine):

After the above, the following is a list of the names of the persons who have been mentioned in the preceding pages. The names are given in the order in which they are mentioned in the text. The names are given in the order in which they are mentioned in the text.

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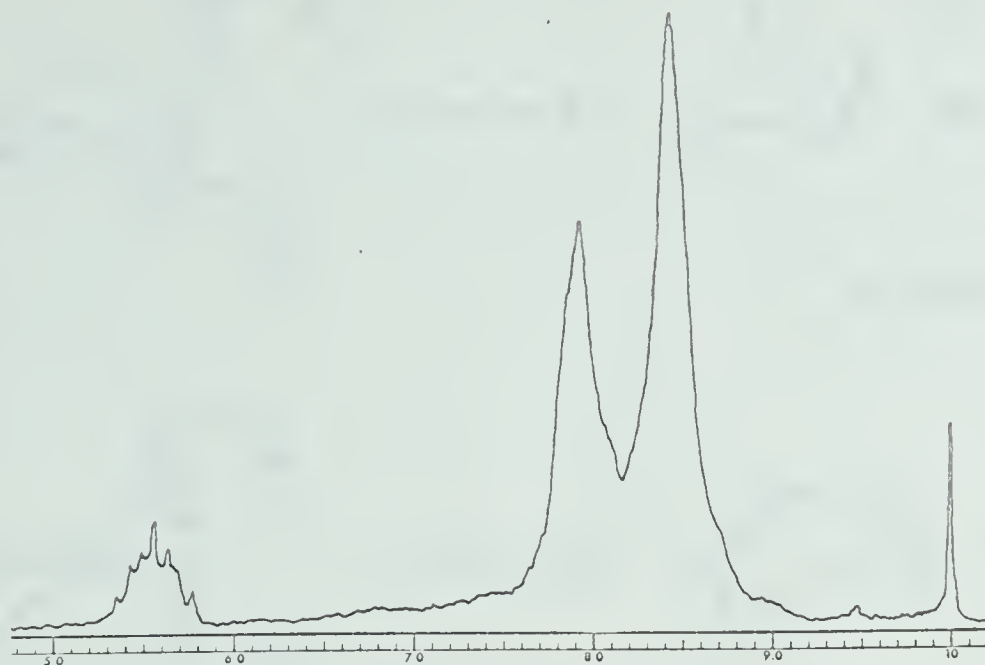


FIG. 5. N.m.r. spectrum (60 Mc.p.s.) of reaction mixture formed after two days from an equimolar solution of iodine in neat cyclohexene.

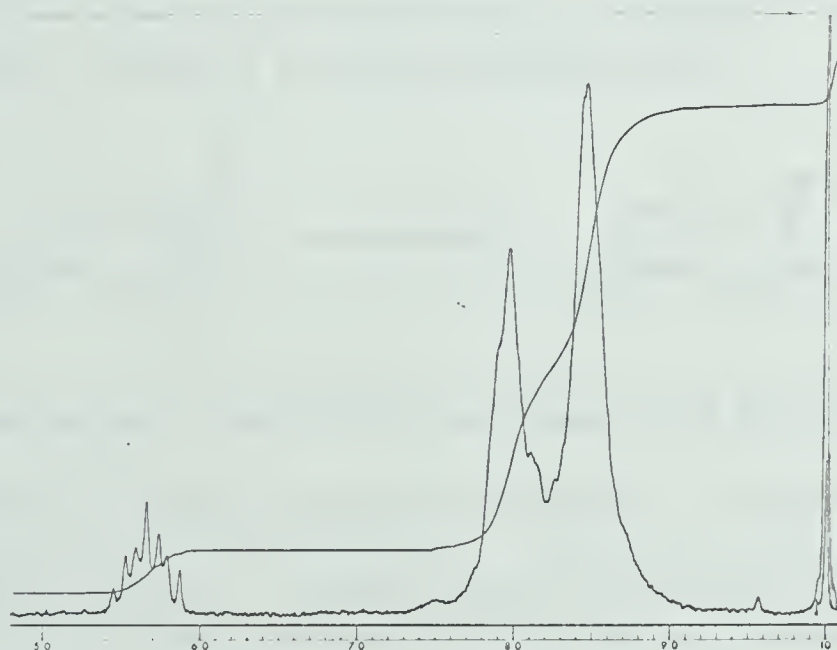
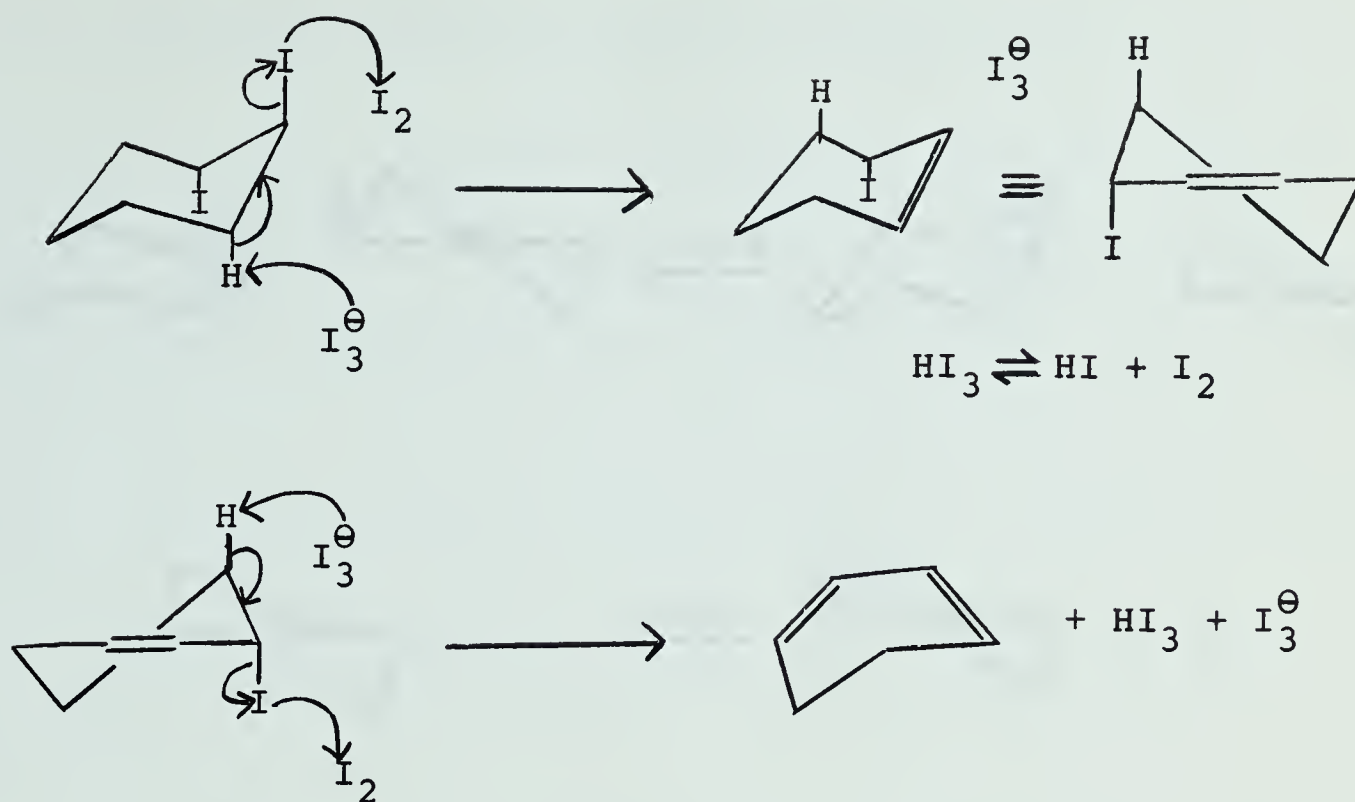
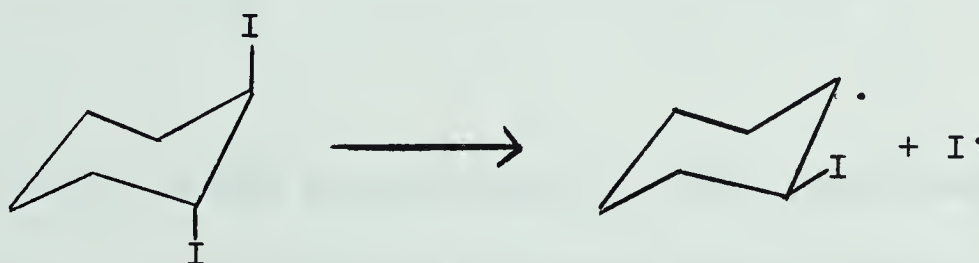


FIG. 6. N.m.r. spectrum (60 Mc.p.s.) of neat cyclohexyl iodide.





Cyclohexyl iodide and hydrogen iodide could, also, conceivably, arise via free radical mechanisms. Cyclohexene diiodide could decompose by homolytic fission of a carbon-iodine bond:



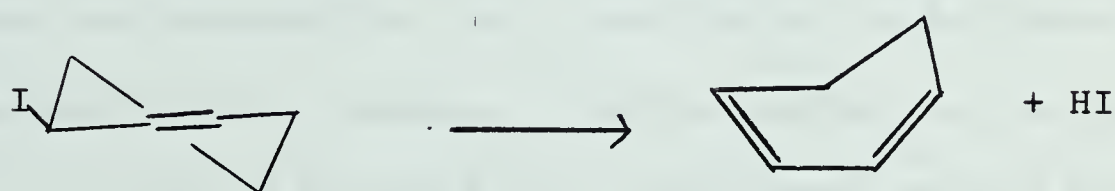
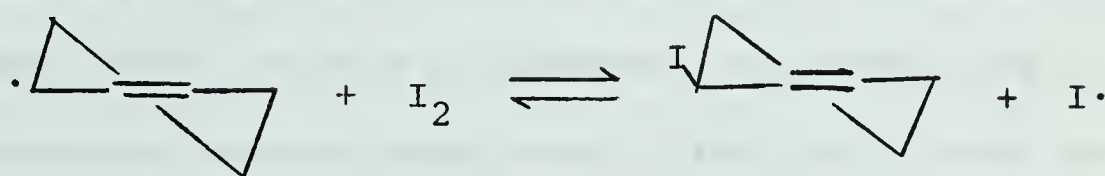
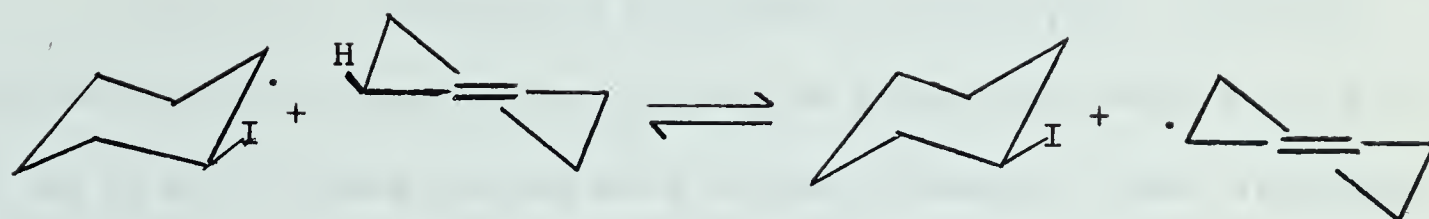
Then, abstraction of an allylic hydrogen from a molecule of cyclohexene by the iodocyclohexyl radical would lead to cyclohexyl iodide and a cyclohexenyl radical. In the presence of excess iodine, the cyclohexenyl radical could form 3-iodocyclohexene which in turn would decompose to 1,3-cyclohexadiene and hydrogen iodide.



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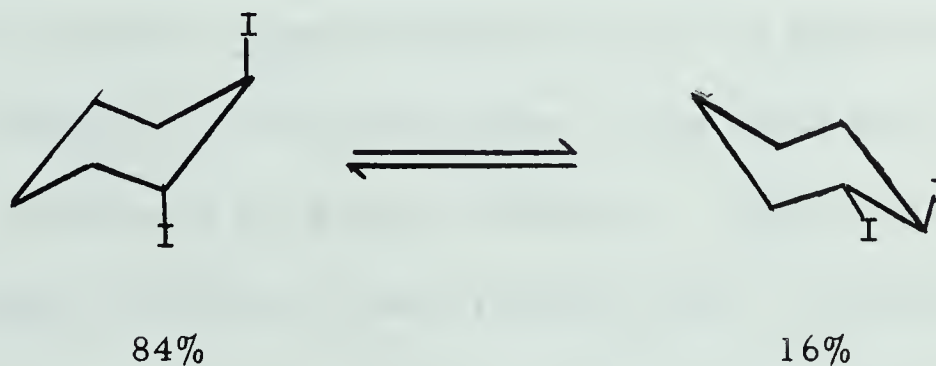
In the presence of high concentrations of iodine, Eberhardt (144) has shown that 1,3-cyclohexadiene undergoes polymerization as the exclusive reaction.

We avoided the above side reaction by using relatively dilute solutions of reactants or by adding iodine to chilled concentrated solutions of cyclohexene or neat cyclohexene. Concentrated solutions of cyclohexene diiodide, when required, were freshly prepared.

Configuration and Conformation of Cyclohexene Diiodide

The n.m.r. spectrum of cyclohexene diiodide {Fig. 3} showed for the methine protons a relatively narrow signal (half-width 9 c.p.s.). If one or both of these protons were in axial orientation, then, according to the Karplus curve (145, 146), a considerably larger amount of splitting and broadening of this signal would be expected. The product of iodine-cyclohexene addition must be cyclohexene trans-diiodide and this compound must exist mainly with the iodine atoms in the diaxial rather than the diequatorial orientation.

These conclusions have been substantiated by Lemieux and Lown (147) who have analyzed the n.m.r. spectrum of 1,4,4-trideuterio-cyclohexene diiodide in benzene. They showed that this compound exists to an extent of about 84% in the conformation wherein both iodines are in diaxial orientation:



The conformational equilibria of several other cyclohexene trans-dihalides have been investigated by means of dipole moment studies and

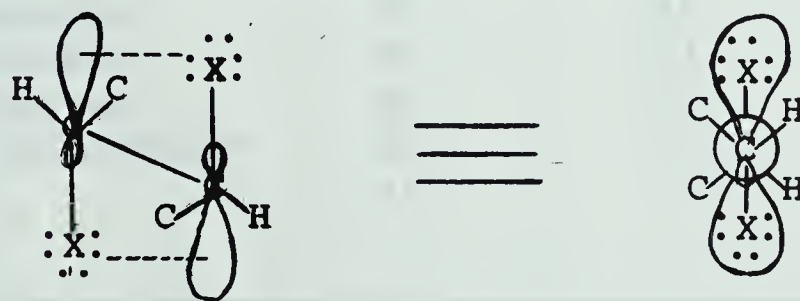
Raman spectra (29, 148, 149) and, more recently, by means of n.m.r. spectroscopy (137, 147, 150). In benzene, the dibromide has been found to exist to an extent of 52-53% in the diaxial conformation, the bromochloride to an extent of 35%, and the dichloride to an extent of 25-29% (29, 149); in carbon tetrachloride or heptane, the diaxial conformer becomes more stable, the above numbers becoming 68%, 56%, and 47%, respectively (29, 149). The effect of other solvents on the conformational equilibrium of these compounds has also been determined (147, 150).

In the solid state, cyclohexene trans-dibromide is believed to exist entirely in the diaxial form and cyclohexene trans-dichloride entirely in the diequatorial form (148). In the gaseous state, however, the dibromide is thought to be only 40% in the diaxial orientation (151). N.m.r. studies at low temperatures have shown that cyclohexene trans-chloroiodide occurs to the extent of 68% in the diaxial conformer. (137)

In cyclohexene trans-dihalides, then, it is apparent that the halogens, chlorine, bromine and iodine, in the order given, have an increasing preference for diaxial orientation. This phenomenon has been attributed to polar and steric factors (150). In diaxial conformation, the two polar carbon-halogen dipoles are in opposite directions, a preferred orientation in nonpolar media; with increasing bulk, the halogens must become more and more crowded in the diequatorial

conformation while at the same time the carbon-halogen bond increases in length and, thereby, reduces cross-ring hydrogen-halogen repulsions in the diaxial conformation. In an undistorted diequatorial conformer, the distance between centers of chlorine atoms is only 3.19 Å while twice the van der Waals radius of chlorine is 3.60 Å; the corresponding distances for the diequatorial conformer of cyclohexene trans-dibromide and of bromine are 3.35 Å and 3.90 Å, respectively (150). The distance between iodine atoms in the gauche conformer of ethylene diiodide is only 3.60 Å (18) while twice the van der Waals radius of iodine is 4.30 Å (152).

It has been recently suggested that the preference of bromine and iodine for diaxial conformation may be rationalized in terms of molecular orbital theory (153-155): mixing between lone pair orbitals of halogen atoms and the antibonding orbitals of the adjacent carbon-halogen bonds may occur:



The overlap would be sterically impossible for the diequatorial conformer.

Extent of Formation of Several Alkyl-substituted
Cyclohexene Diiodides and of Cyclopentene Diiodide

It was of interest to determine the effect on the extent of diiodide formation of substituents on the cyclohexene ring. Accordingly, under the same conditions used previously for cyclohexene (reactants, 2.0 M in solution in carbon tetrachloride) iodine was allowed to react with the alkyl-substituted cyclohexenes listed in Table IV and, also, with cyclopentene.

TABLE IV

Extent of cycloalkene-iodine addition by n.m.r. spectroscopy
in carbon tetrachloride, reactants, 2.0 M

Cycloalkene	Percent reaction ^a	K _{Eq'} liter/mole	- Δ F, kcal/mole
Cyclohexene	84	16	1.7
4-Methylcyclohexene	83	15	1.6
3-Methylcyclohexene	82	13	1.5
4-t-Butylcyclohexene	79	9	1.3
4,4-Dimethylcyclohexene ^b	20		
Cyclopentene	72	5	0.9

^aThe reaction was performed at about 25° but the temperature of the probe in the spectrometer was about 38°

^bIn this case solution was not attained; the spectrum was obtained on the supernatant liquor.

The n.m.r. spectra of the cycloalkenes and of the reaction solutions, at equilibrium, are presented in Figures 1, 2, 7-16. In all cases, a new signal or signals up field from those due to the ethylenic protons of the cycloalkene appeared in the n.m.r. spectra when iodine was added to the alkene. These new signals taken as evidence of cycloalkene diiodide formation were assigned to the methine protons of the diiodides, and their intensities relative to the intensities of the signals for ethylenic protons gave a direct measurement of the ratio of cycloalkene diiodide to cycloalkene. The extents of cycloalkene-iodine addition are given in Table IV, along with the equilibrium constants for the reactions, calculated from the equation,

$$K_{Eq} = \frac{(\text{Diiodide})_{Eq}}{(I_2)_{Eq}(\text{Alkene})_{Eq}}$$

where the concentrations of product and reactants are the equilibrium concentrations (moles per liter). The free energy change, for each of the reactions was calculated from the equation (156),

$$-\Delta F = RT \ln K_{Eq},$$

and the calculated values are also presented in Table IV.

At lower concentrations (0.050 M) of reactants in carbon tetrachloride, the extent of cycloalkene-iodine addition was determined iodometrically at 0.0° and at 25.0°; the percentage reaction and the equilibrium constant for each of the reactions are given in Table V.

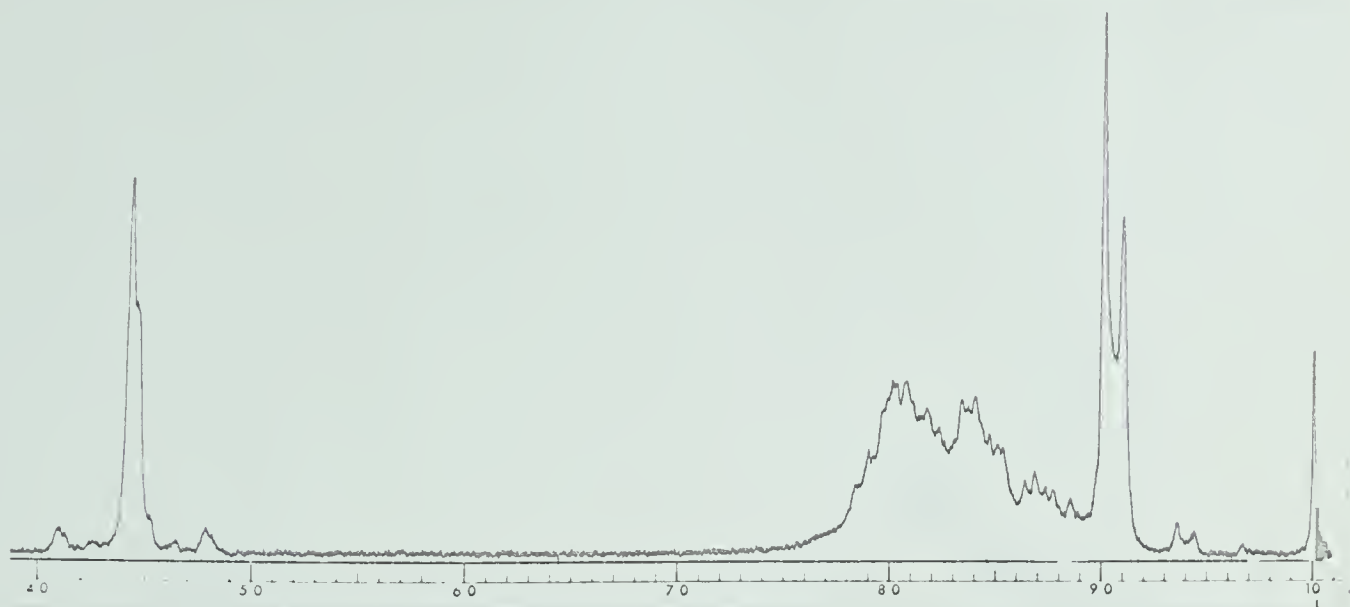


FIG. 7. N.m.r. spectrum (60 Mc.p.s.) of 4-methylcyclohexene, 50% (v/v) in carbon tetrachloride.

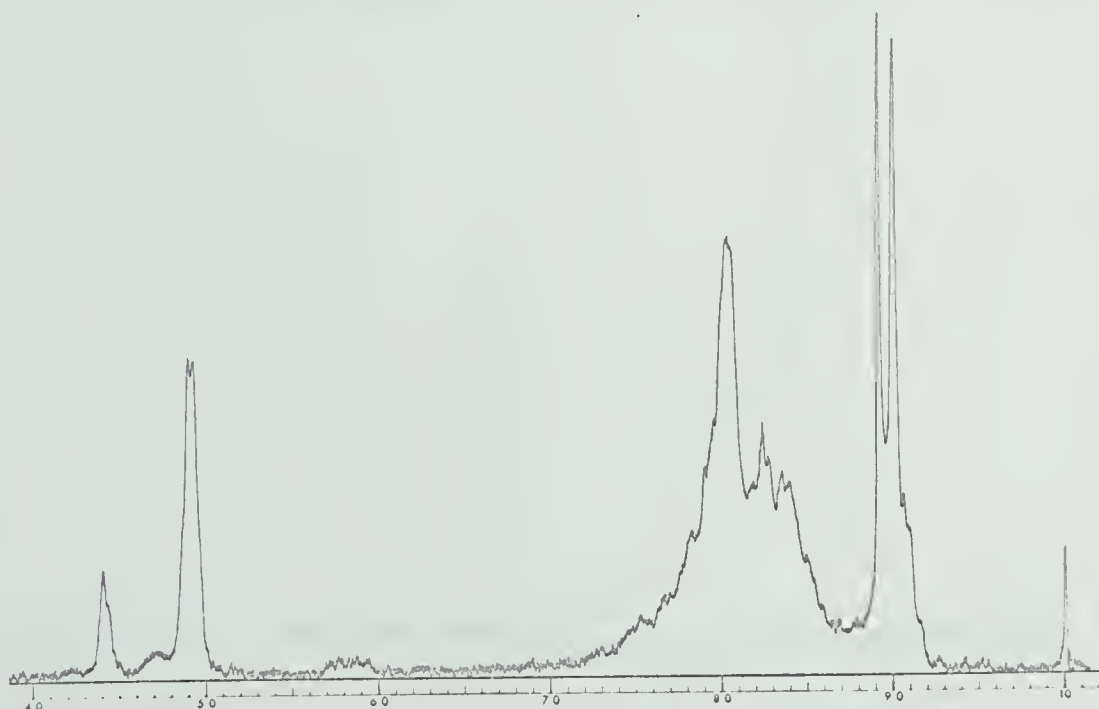


FIG. 8. N.m.r. spectrum (60 Mc.p.s.) of 4-methylcyclohexene-iodine-4-methylcyclohexene diiodide equilibrium mixture in carbon tetrachloride. 4-Methylcyclohexene and iodine, initially, 2.0 M. Extent of formation of diiodide, 83%.

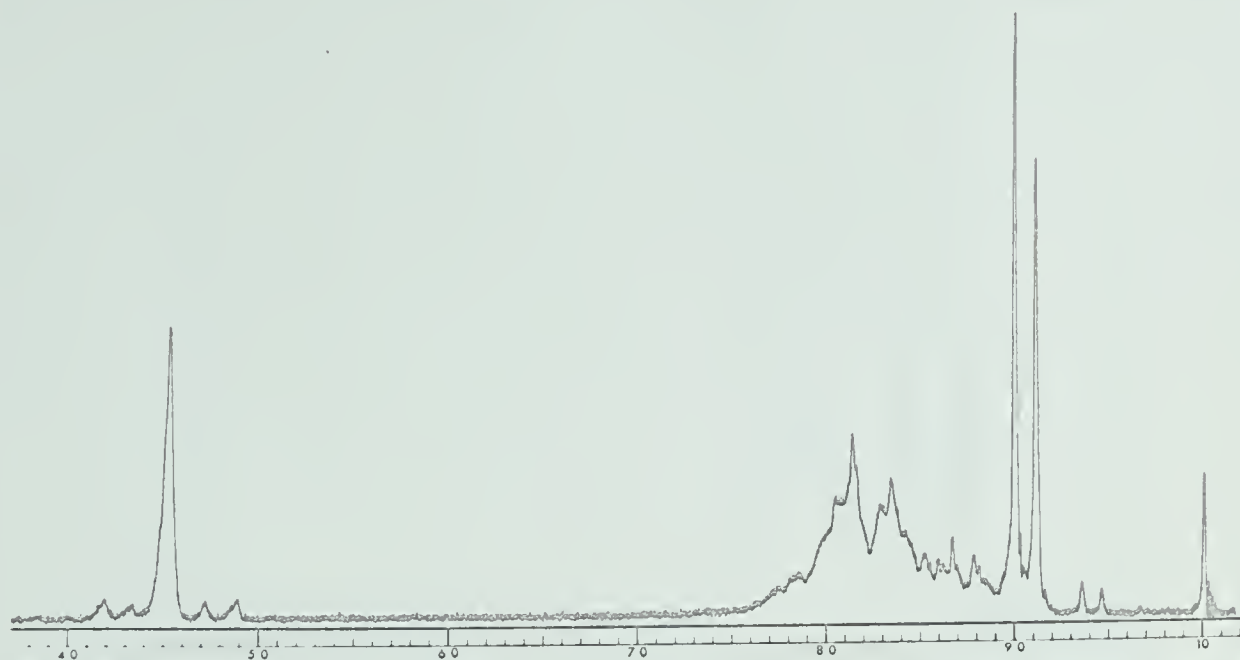


FIG. 9. N.m.r. spectrum (60 Mc.p.s.) of 3-methylcyclohexene, 50% (v/v) in carbon tetrachloride.

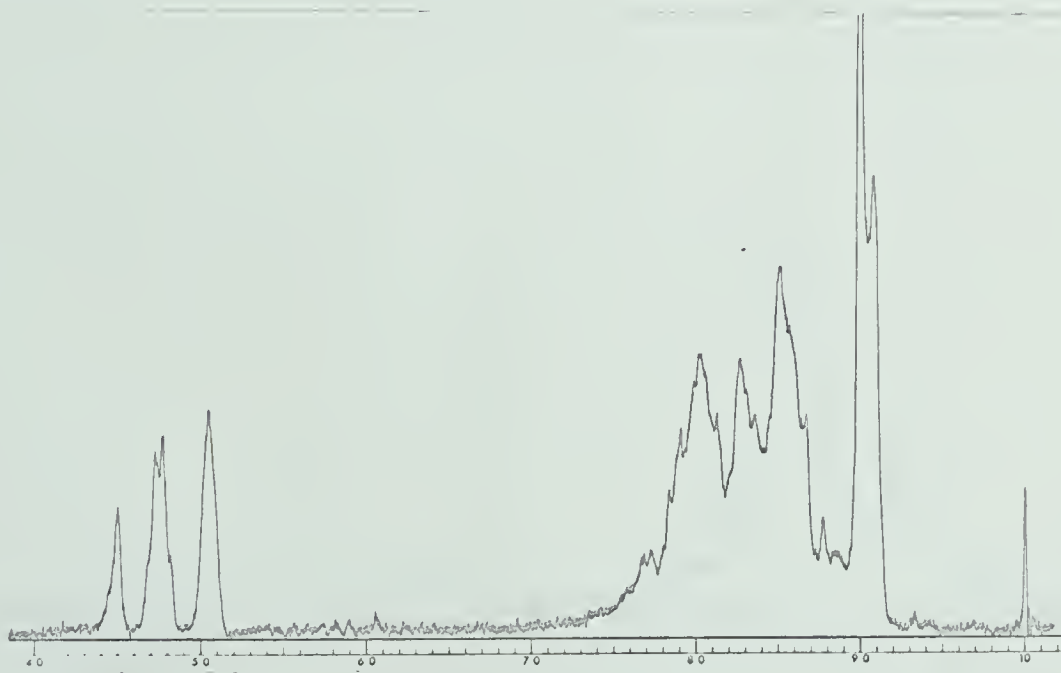


FIG. 10. N.m.r. spectrum (60 Mc.p.s.) of 3-methylcyclohexene-iodine-3-methylcyclohexene diiodide equilibrium mixture in carbon tetrachloride. 3-Methylcyclohexene and iodine, initially, 2.0 M. Extent of formation of diiodide, 82%.



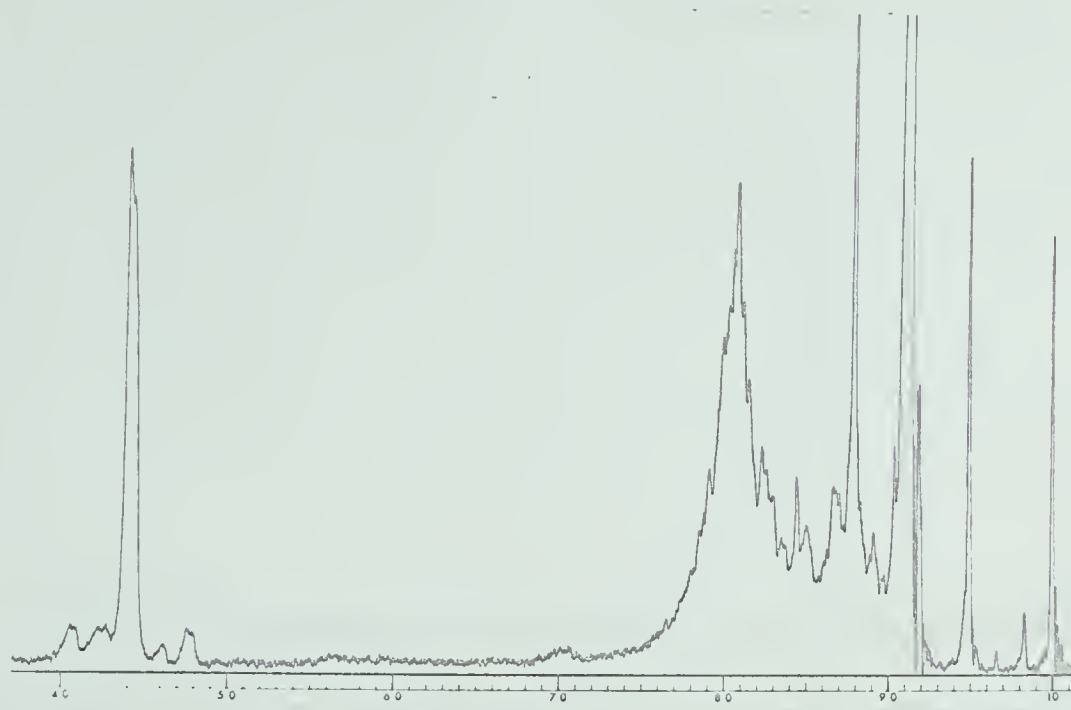


FIG. 11. N.m.r. spectrum (60 Mc.p.s.) of 4-t-butylcyclohexene, 50% (v/v) in carbon tetrachloride.

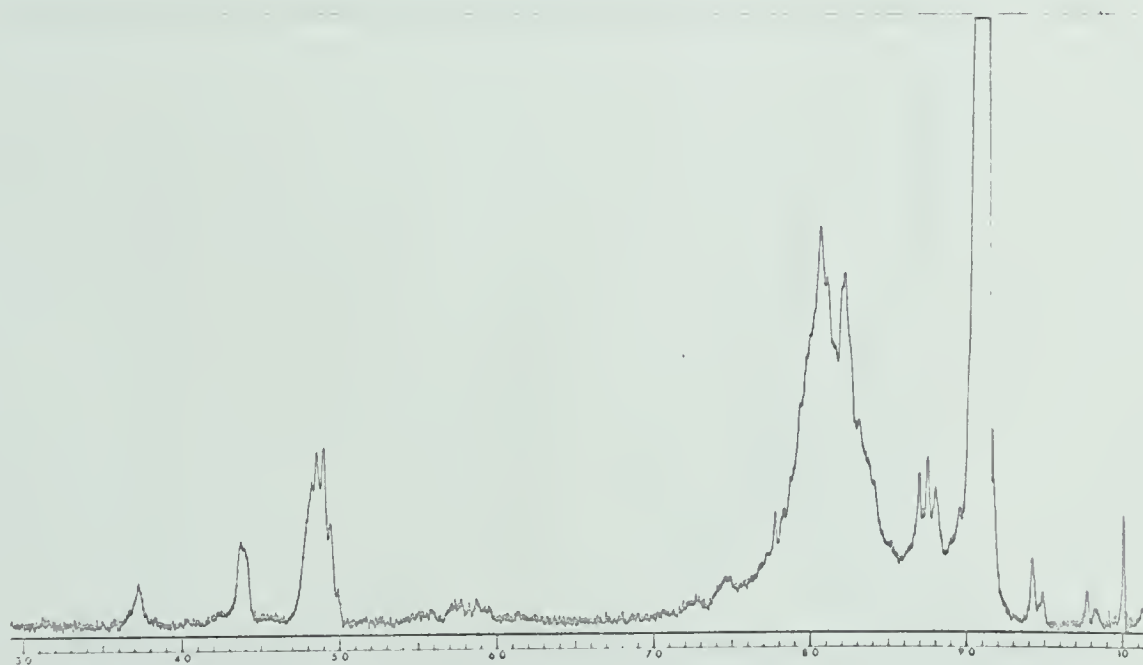


FIG. 12. N.m.r. spectrum (60 Mc.p.s.) of 4-t-butylcyclohexene-iodine-4-t-butylcyclohexene diiodide equilibrium mixture in carbon tetrachloride. 4-t-butylcyclohexene and iodine, initially, 2.0 M. Extent of formation of diiodide, 79%.

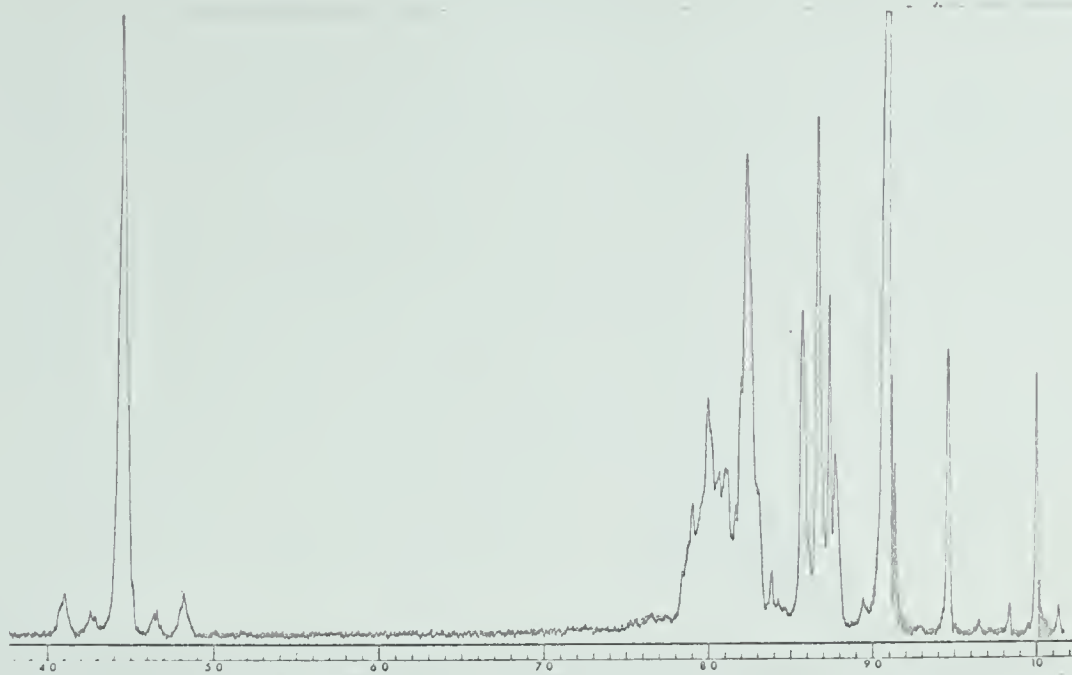


FIG. 13. N.m.r. spectrum (60 Mc.p.s.) of 4,4-dimethylcyclohexene, 50% (v/v) solution in carbon tetrachloride.

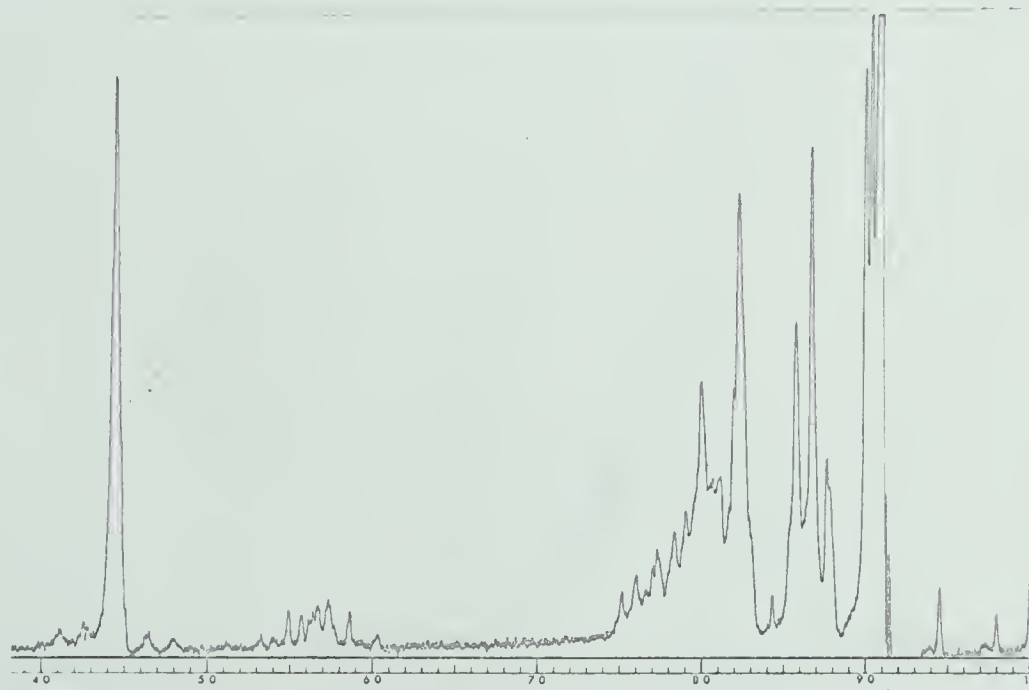


FIG. 14. N.m.r. spectrum (60 Mc.p.s.) of 4,4-dimethylcyclohexene-iodine-4,4-dimethylcyclohexene diiodide equilibrium mixture in carbon tetrachloride. 4,4-Dimethylcyclohexene and iodine, initially 2.0 M. Extent of formation of diiodide, 20%.

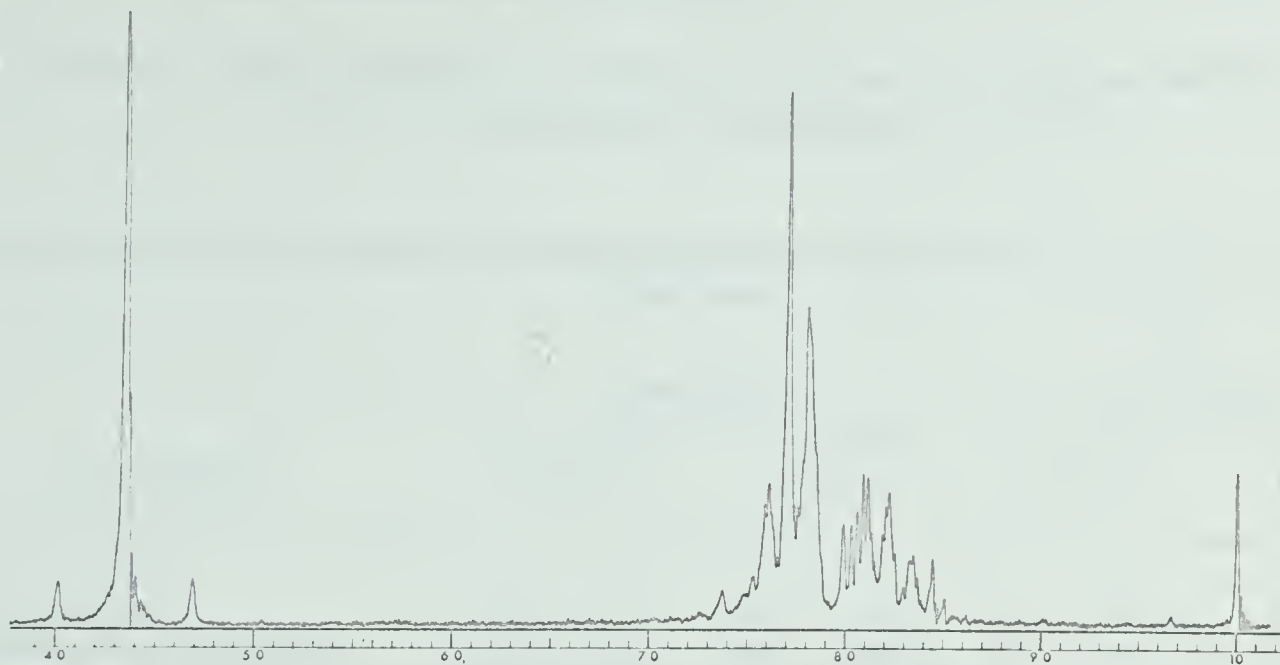


FIG. 15. N.m.r. spectrum (60 Mc.p.s.) of cyclopentene, 50% (v/v) solution in carbon tetrachloride.

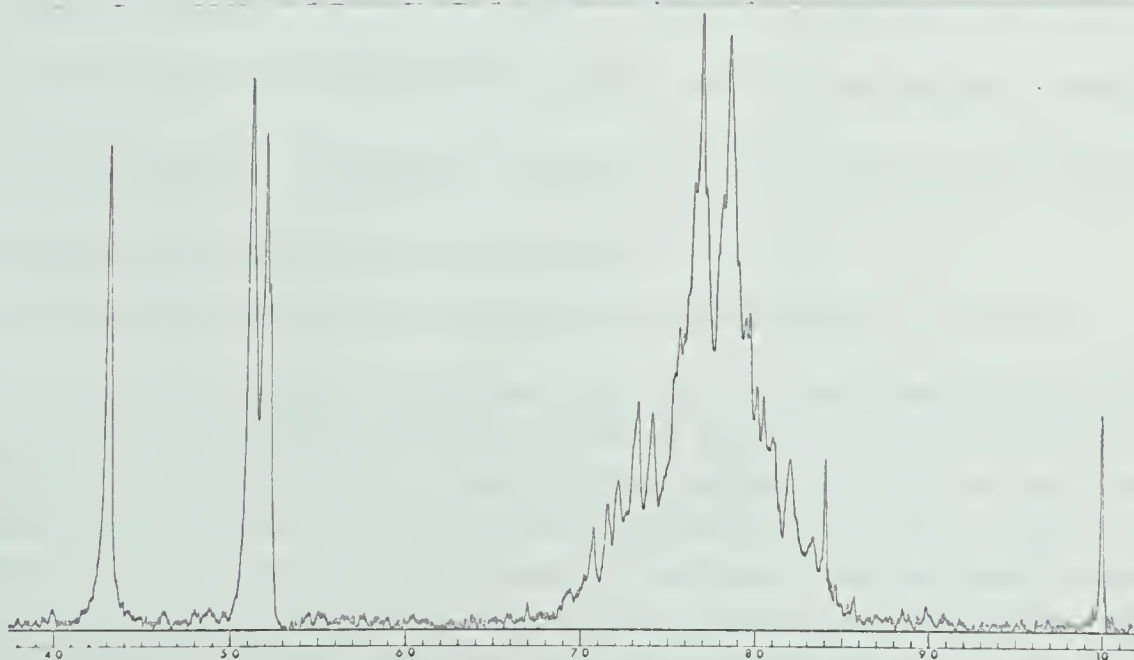


FIG. 16. N.m.r. spectrum (60 Mc.p.s.) of cyclopentene-iodine-cyclopentene diiodide equilibrium mixture in carbon tetrachloride. Cyclopentene and iodine, initially, 2.0 M. Extent of formation of cyclopentene diiodide, 72%.

TABLE V

Iodometric determination of extent of cycloalkene-iodine addition
in carbon tetrachloride, reactants, 0.050 M

Cycloalkene	Percent		K_{Eq} ,	
	reaction		liter/mole	
	25.0 ^o ^a	0.0 ^o ^b	25.0 ^o ^a	0.0 ^o
Cyclohexene	57.0, 57.4	78.7, 78.7	61.7, 63.2	346
4-Methylcyclohexene	53.5, 52.7	74.7, 75.2	49.2, 47.0	240
3-Methylcyclohexene	52.0, 52.3	73.8, 74.7	45.2, 46.1	225
4-t-Butylcyclohexene	42.6	62.1, 63.1	25.9	89.5
4,4-Dimethylcyclohexene	8.0, 7.5	20.2, 21.5	1.9, 1.8	6.7
Cyclopentene	30.0, 34.2	57.9, 58.9	12.2, 15.8	67.5

^aExcept for 4-t-butylcyclohexene, duplicate experiments performed.

^bDuplicate analyses but same reaction solution in each case.

At both concentrations the same trend in percentage reaction and values of equilibrium constants occurs; hence, the two methods of determination substantiate one another.*

*In cyclohexene-iodine addition with the initial concentrations of reactants 2.0 M, in order for the value of K_{Eq} to be 62.5 liter/mole, the reaction would have to proceed to the extent of 92% rather than to the extent of 84% found. In this case at the equilibrium found, the relative molar amounts of cyclohexene, iodine, cyclohexene diiodide, and carbon tetrachloride were 2 : 2: 8: 20, respectively. On the other hand, in the case involving initial concentrations of reactants of 0.050 M, at equilibrium, the relative amounts of the above compounds were 2: 2: 3: 1000, respectively. Thus, the difference in the values of K_{Eq} in the two cases is probably due to a difference in medium. (For other solvent effects, see p. 62).

For cyclohexene-iodine addition, the equilibrium constant was determined at five degree intervals from 0.0-35.0°. The equilibrium constants and the corresponding free energy changes are given in Table VI.

TABLE VI

Variation in percentage reaction, equilibrium constant, and free energy change for cyclohexene-iodine addition in carbon tetrachloride, reactants, 0.050 M over temperature range 0.0 - 35.0 °

Temp (°C)	Percent reaction ^a	K _{Eq} , liter/mole	- Δ F, kcal/mole
0.0	77.7, 78.7	313, 346	3.14, 3.19
5.0	74.7, 73.5	233, 209	3.03, 2.88
10.0	70.5, 70.7	162, 164	2.88, 2.88
15.0	66.7, 66.0	120, 114	2.76, 2.73
20.0	63.5, 60.5	95.3, 77.7	2.66, 2.55
25.0	57.5, 57.5	63.5, 63.5	2.48, 2.48
30.0	53.4, 53.3	49.2, 48.9	2.36, 2.36
35.0	48.7, 49.1	37.0, 37.9	2.22, 2.24

^aDuplicate analyses on same reaction solution.

The enthalpy change, ΔH, and the entropy change, ΔS, for a reaction may be obtained from the equations (156),

$$\Delta H = \frac{\Delta(\Delta F/T)}{\Delta(1/T)} \quad \text{and} \quad \Delta S = \frac{\Delta H - \Delta F}{T}.$$

From the slope of a plot of ΔF/T versus 1/T (Fig. 17) the enthalpy change for cyclohexene-iodine addition was found to be -10.0 kcal/mole and the entropy change -25.2 kcal/mole.

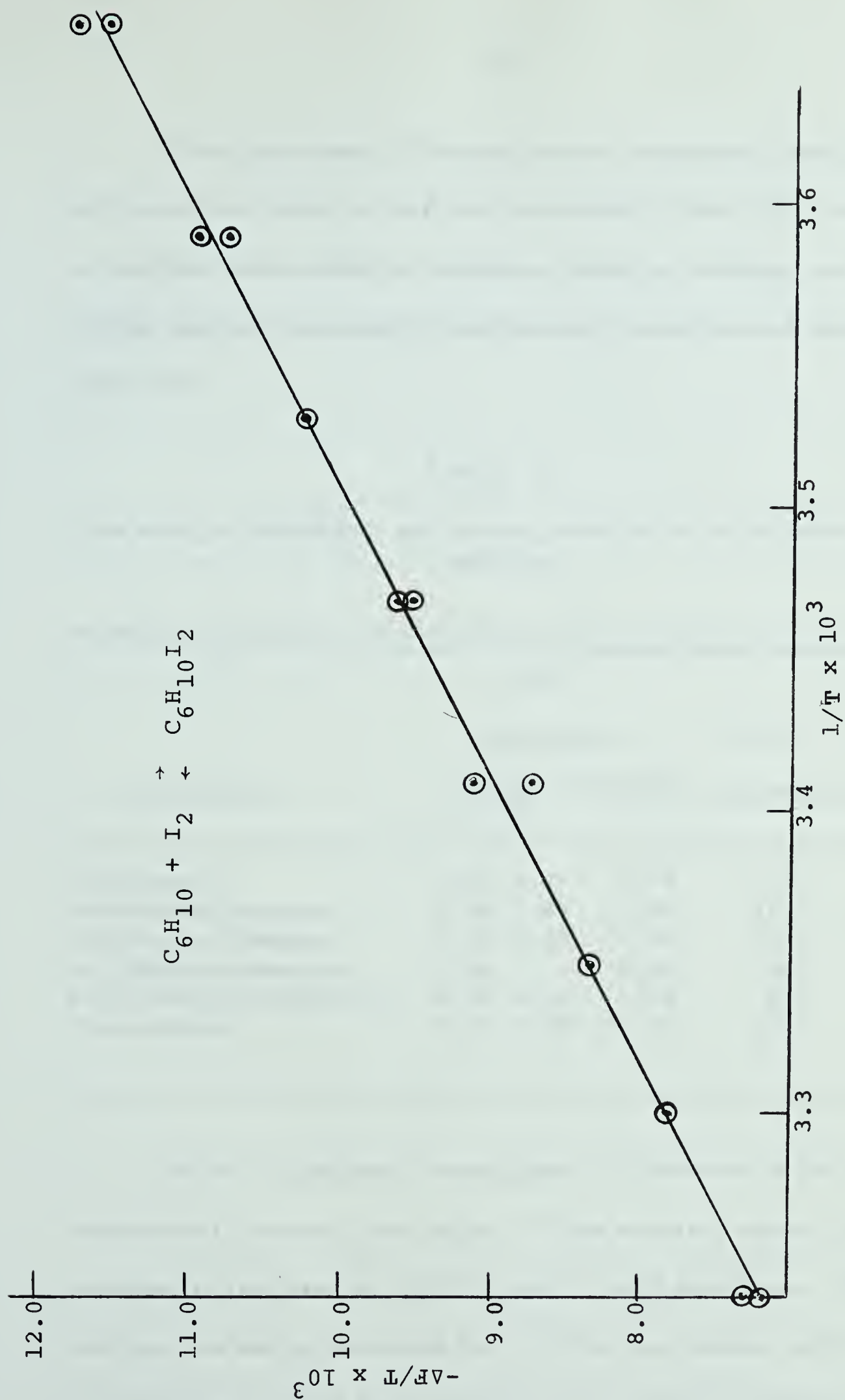


FIG. 17. $-\Delta F/T$ vs. $1/T$ for cyclohexene-iodine addition in carbon tetrachloride, reactants, 0.050 M.

From the values of the equilibrium constants (Table V), the corresponding values of $-\Delta F$ are presented in Table VII; for each cycloalkene-iodine addition reaction a value for enthalpy and entropy change has been calculated from the above equations and included in Table VII.

TABLE VII

Free energy, enthalpy, and entropy changes in cycloalkene-iodine addition

Cycloalkene	$-\Delta F,$		$-\Delta H$ kcal/mole	$-\Delta S$ cal/mole/deg
	kcal/mole			
	25.0°	0.0°		
Cyclohexene	2.46, 2.47	3.19	11.0	28.6
4-Methylcyclohexene	2.32, 2.29	2.99	10.3	26.8
3-Methylcyclohexene	2.27, 2.28	2.95	10.2	26.5
4-t-Butylcyclohexene	1.94	2.45	8.0	20.5
4,4-Dimethylcyclohexene	0.38, 0.35	1.04	8.3	26.5
Cyclopentene	1.49, 1.65	2.30	10.2	28.9

Of the cycloalkenes investigated, cyclohexene is the one which reacts most favorably with iodine. Even with this alkene, however, the decrease in free energy at 25° is only 1.7-2.5 kcal/mole. The corresponding free energy decrease for bromine-cyclohexene addition is 30 kcal/mole (157) so that in terms of free energy change the addition

of bromine to cyclohexene is more than ten times as favorable as iodine addition. The same situation holds true for cyclopentene, the free energy decreases for iodine addition and bromine addition, being 0.9-1.5 and 26 kcal/mole (157), respectively.

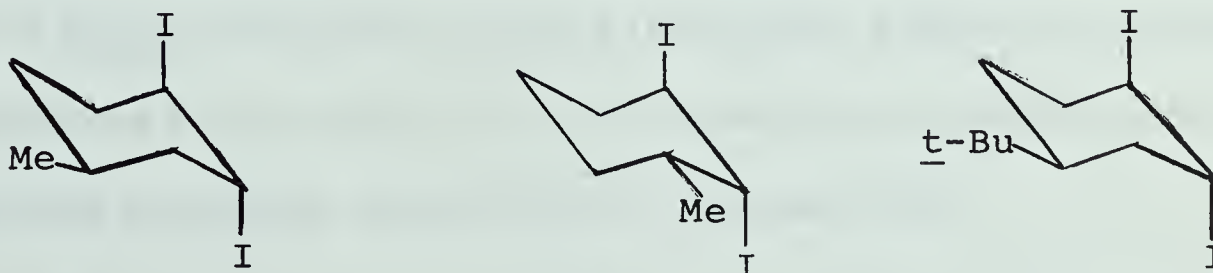
Our calculated values for ΔH show the cycloalkene-iodine addition reaction to be exothermic by 8-10 kcal/mole. As previously noted, Birckenhauer (16) found ΔH for the addition of iodine to cyclohexene in benzene to be -7.86 kcal/mole while Walling (60) and Sherman et al (100, 101) theoretically calculated the enthalpy decrease for iodine-ethylene addition to be 6-8 kcal/mole.

The negative entropy changes found for cycloalkene-iodine addition are to be expected since the combination of two molecules to form a single, and, conformationally, rather rigid compound must involve an increase in order. With the exception of the formation of 4-t-butylcyclohexene diiodide, the entropy decrease is 25-29 cal/mole-degree. The smaller decrease found for 4-t-butylcyclohexene-iodine addition (20.5 kcal/mole-degree) must be due to the relatively rigid conformation of 4-t-butylcyclohexene, i.e., there is a smaller increase in order in this reaction.

The extent of formation of the diiodide of an alkyl-substituted cyclohexene relative to that for cyclohexene must depend on the availability of a favorable conformation for the cycloalkene diiodide. A favorable

conformation would be one in which the alkyl substituent can readily occupy an equatorial orientation (158) and the iodine atoms diaxial orientation (147). The n.m.r. spectra (Figures 8, 10, and 12) of the diiodides of the monoalkyl-substituted cycloalkenes which we have investigated show relatively narrow absorption signals [as was the case for cyclohexene (147)] for the methine protons geminal to iodine. According to the Karplus relationship (145-147), relating dihedral angle to coupling constant for vicinal protons, these monoalkyl-substituted cycloalkene diiodides must occur largely in a conformation in which the iodine atoms are diaxially orientated. (The n.m.r. spectrum of trans-3-cis-4-dibromo-t-butylcyclohexane (122), it may be noted, has an absorption signal for the methine protons geminal to bromine of base width 23 c.p.s. whereas the signal in the n.m.r. spectrum (Fig. 12) for the methine protons geminal to iodine in 4-t-butylcyclohexene diiodide has a base width of only 20 c.p.s.)

It follows, then, that these cycloalkene diiodides must be formed mainly with the following configuration and conformation.



The cycloalkene diiodides with the alkyl groups in the the opposite orientation to that given in the above structures would be configurational isomers; conceivably, these isomers could form but they would be expected to be much less favorable than the structures depicted.

The data in Tables IV, V, and VII reveal the extent of cycloalkene-iodine addition decreases little by the insertion of a methyl substituent at carbon-3 or carbon-4, the decrease in $-\Delta F$ being only 0.2 kcal/mole. Even the replacement of a hydrogen by a t-butyl group at carbon-4 decreases $-\Delta F$ by only 0.5-0.7 kcal/mole. Cyclohexene diiodide can, therefore, it appears, easily accommodate alkyl substituents in equatorial orientation at carbon-3 or carbon-4.

Relative to cyclohexene or 4-methylcyclohexene, the addition of iodine to 3-methylcyclohexene might be expected to be hindered by the gauche interaction between the 3-methyl and the 2-iodine substituents. Although the gauche interaction in 3-methylcyclohexene diiodide may in some way account for the large chemical shift (18 c.p.s.) between the 1- and 2-protons in its n.m.r. spectrum (Fig. 10), no significant decrease in the extent of diiodide formation has been found. It may be that the gauche interaction resulting from iodine addition is adequately counteracted by the relief of the steric interference recently found to be associated with allylic substituted cyclohexenes (159).

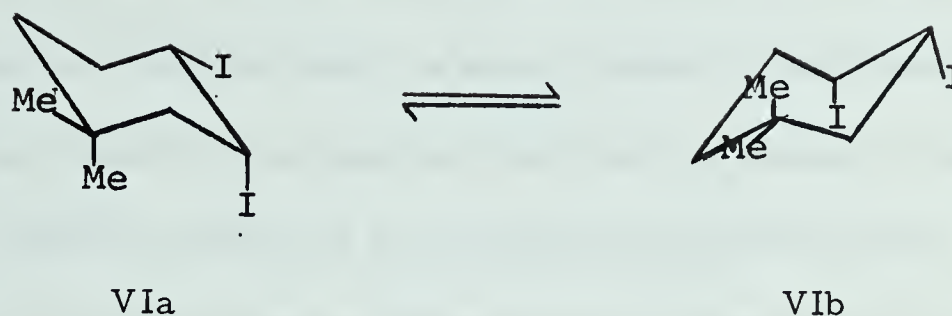
The insertion of two methyl groups on carbon-4 of cyclohexene

allows the formation of only one possible product (V) upon trans-addition of iodine; for this product, as for cyclohexene trans-diiodide, there are two possible chair conformations:



Conformer Va, although it has the iodine atoms in the favored diaxial orientation, has an axial methyl group on carbon-4 in position for a strong cross-ring repulsion of the iodine atom on carbon-2. Conformer Vb avoids this cross-ring repulsion but has the iodine atoms in diequatorial arrangement, an unfavorable arrangement (147). In view of the lack of a favorable conformation for 4,4-dimethylcyclohexene diiodide, it is not surprising that, relative to cyclohexene, 4,4-dimethylcyclohexene was found to react with iodine to a relatively small extent, the decrease in $-\Delta F$ on going from cyclohexene to 4,4-dimethylcyclohexene, being, in fact, greater than 2 kcal/mole (Table VII).

A cis-addition of iodine to 4,4-dimethylcyclohexene would result, also, in only one possible product (VI) for which there are two possible chair conformations:

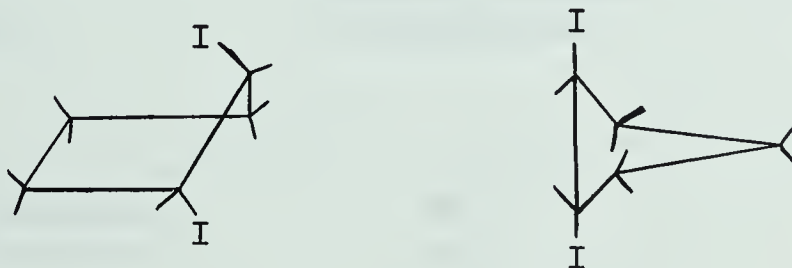


Neither VIa nor VIb has the iodine atoms in their favored diaxial orientation; conformer VIb, however, avoids cross-ring repulsions between substituents and would, therefore, be the more favorable structure. Regarding cross-ring repulsions between substituents and hydrogens, VIb would be expected to be more strained than VIa since the former has an axial iodine whereas the latter has not. On this basis, then, trans-addition would be expected to be more favorable than cis-addition.

The n.m.r. spectrum (Fig. 14) of 4,4-dimethylcyclohexene diiodide does, indeed, support the idea that trans-addition rather than cis-addition occurs. The relatively narrow absorption signals (base width of 15-20 c.p.s.) found in the case of cyclohexene and the mono-alkyl substituted cyclohexene diiodides for the methine protons geminal to iodine are in this case replaced by a broad multiplet (base width of 45 c.p.s.) which from the Karplus relationship (145-147) indicates that the protons in 4,4-dimethylcyclohexene diiodide geminal to iodine are in diaxial orientation (VIb).

The formation of cyclopentene diiodide is only about 0.9 kcal/mole less favorable than the formation of cyclohexene diiodide (Table VII). Hence, cyclopentene diiodide must be able to adopt a conformation in which the vicinal iodine atoms approach the favored diaxial orientation.

Dipole moment studies of cyclopentene trans-dibromide have indicated that the vicinal bromine atoms favor a quasi-diaxial orientation (158). Since iodine atoms have a greater tendency than bromine atoms for diaxial orientation, then, cyclopentene trans-diiodide must predominate in a conformation such as represented by one of the following structures (158).



The n.m.r. spectrum (Fig. 16) of cyclopentene diiodide showed a doublet for the methine protons geminal to iodine. Each methine proton would be expected to be coupled with two methylenic protons; the fact that further splitting was not observed in the spectrum is probably due to the existence of unequal dihedral angles between the methine protons and the adjacent methylenic protons.

Effect of Solvent on Equilibrium Constant
in Cyclohexene-Iodine Addition

The percentage reaction and the equilibrium constant for cyclohexene-iodine addition in a variety of solvents was determined iodometrically and the results are presented in Table VIII. The extent of cyclohexene-iodine addition that occurs in carbon tetrachloride or methylene chloride

TABLE VIII

Equilibrium constants in various solvents at 25.0°
for the addition of iodine to cyclohexene.
Each reactant initially 0.050 M.

Solvent	Percent reaction at equilibrium	Equilibrium constant, liter/mole
Carbon tetrachloride	57.0	61.7
Methylene chloride	56.5	60.2
Nitrobenzene	51.0	42.5
Benzene	40.0	22.2
Mesitylene	40.0	22.2

is much greater than that in benzene and mesitylene (1,3,5-trimethylbenzene). Conceivably, this situation may be due to complexing of iodine with the aromatic solvent (160, 161) which would tend to shift the cyclohexene diiodide-cyclohexene-iodine equilibrium towards the side of cyclohexene and iodine.

The extent of reaction was also determined in nitrobenzene. Although this is an aromatic compound, it differs from benzene and mesitylene in that it is a very polar solvent; also, the presence of an electron-withdrawing substituent on the aromatic nucleus would be expected to make it a poorer iodine-complexing solvent (161). In any case, the reaction was found to proceed further in nitrobenzene than in the other aromatic solvents.

Evidence for Homolytic Cyclohexene-Iodine Addition in Inert Non-polar Solvents

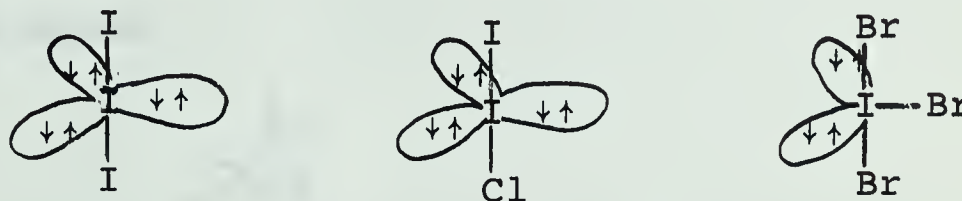
Alkenes are known to attract electrophilic iodine with the resultant formation of so-called pi-complexes (162-168). We found when solutions of iodine, 0.01 M, and cyclohexene, 0.05 M, were prepared in the dark, using undegassed solvent, that 3 or 4% of the iodine rapidly underwent reaction; this observation was made by measuring the intensity of the absorption peak for iodine at 517 m μ and comparing it to the intensity expected if no reaction had occurred. The observed drop in absorbency at 517 m μ was accompanied by the appearance of a new peak at about 315 m μ whose extinction coefficient, based on the amount of iodine reacting, was calculated to be about 7500; for iodine in carbon tetrachloride λ_{max} is about 930 (160). These observations are in accord with the formation of a cyclohexene-iodine charge-transfer complex (162-168).

The ready formation of iodine-alkene complexes suggests that the formation of alkene diiodides from iodine and alkene proceeds via these structures. Using illumination to promote alkene diiodide formation, we observed the changes that occurred in the visible and ultraviolet spectrum of dilute solutions of iodine and cyclohexene in carbon tetrachloride. The absorption maximum in the ultraviolet region gradually moved to lower wavelengths as the band at 517 m μ in the visible region decreased in intensity. Eventually, at equilibrium, the absorption band in the ultraviolet region had its maximum at 275 m μ with an extinction coefficient about 850. The absorption near 275 m μ is in the region expected for alkene diiodides; due to an $n \rightarrow \sigma^*$ transition of an electron on iodine (140), the carbon-iodine bond absorbs in this region.

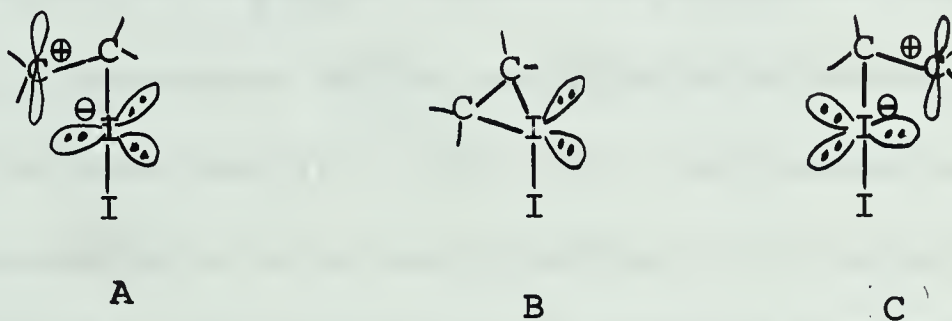
Since alkene-iodine complexes must always be present in inert non-polar solvents whenever iodine and alkene are present, we postulate that the initial intermediate in alkene-iodine addition, whether the overall addition process involves homolytic or heterolytic steps, must be a pi-complex between iodine and alkene.

Related to these complexes are the complexes that iodine forms with halide ion, such as I_3^\ominus and I_2Cl^\ominus (169). Iodine is capable of expanding its valence shell to hold ten electrons (169) and in these trihalides, which are linear structures, iodine is the central atom and the one bearing the excess electrons. Iodine trihalides such as IBr_3 , have a related structure,

the iodine atom being the central trivalent atom (169). The bipyramidal structure of these polyhaldides and polyhalogens may be represented as follows (169).

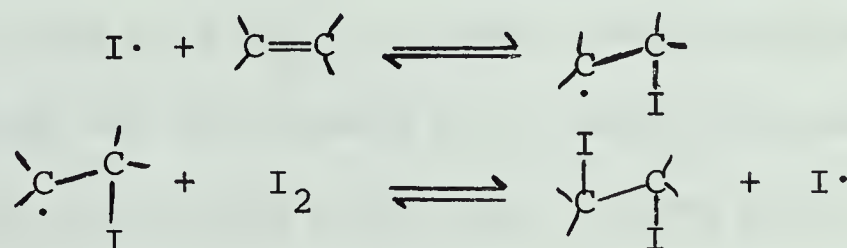


By analogy to the structures of trihalide ions and iodine trihalides, the initial complex formed between alkene and iodine would be expected to be a resonance hybrid of the structures A, B, and C, below. In the absence

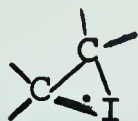


of ion-stabilizing forces, the cyclic structure (B) would be expected to be the main contributor. Also, for unsymmetrical alkenes, structures A and B would not be expected to contribute equally. The structure B has, in fact, been previously discussed as a possible intermediate in halogen-alkene addition by de la Mare (34) and by Hine and Brader (25).

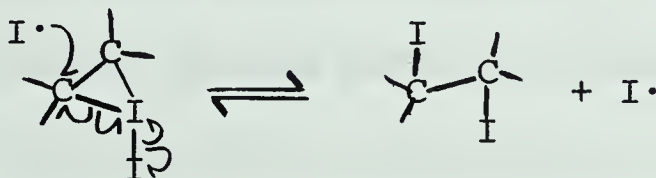
Homolytic iodine-alkene addition has been proposed to occur by direct attack of an iodine atom on alkene followed by abstraction of a second iodine atom from a molecule of iodine by the iodoalkyl radical intermediate (21):



To account for stereospecific trans-addition, Skell and Pavalis (3) have proposed that the iodoalkyl radical intermediate in the above process exists as a bridged radical:



Bridged radicals have been proposed in a number of reactions involving β -haloalkyl radical intermediates (3, 116-123); recently, however, some of the results originally presented as evidence of bridged radicals have been re-interpreted and the possibility of the formation of such species is in some doubt (116, 124, 125). Our postulation that the initial intermediate in iodine-alkene addition is a π -complex is readily seen to account for trans-addition: the attacking free radical species is forced to approach the π -complex from the side of the complex opposite to which the iodine molecule is located:



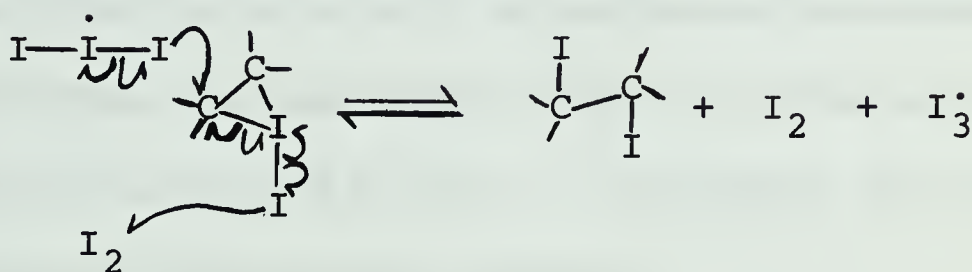
This mechanism differs from the postulate of a bridged free radical in that the loss of an iodine atom from one side of the intermediate occurs simultaneously with the attack of an iodine radical from the opposite side.

In analogy with the triiodide ion, it seems reasonable to suggest that iodine may complex with iodine atoms to form a linear triatomic

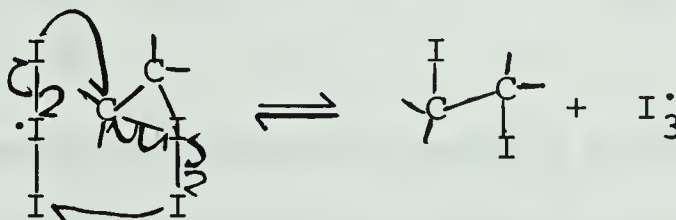
species with the odd electron being located on the central iodine atom:



If iodine radical is complexed in this manner, then, the following mechanism becomes plausible.

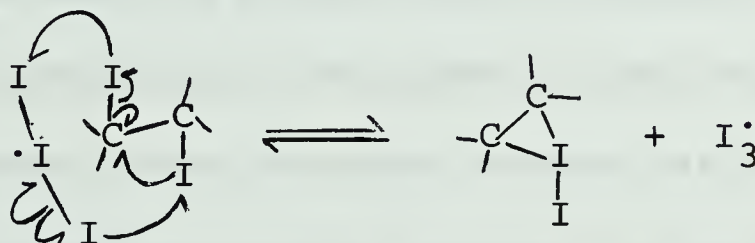


The above reaction is represented as a concerted reaction in which as $\text{I}_3\cdot$ attacks from one side, an iodine atom is split off from the other side and captured by a molecule of iodine; however, these atomic movements may occur consecutively in any of the possible sequences. Dimensionally, it would be possible for alkene diiodide formation to pass through a six-membered cyclic-transition state in which only $\text{I}_3\cdot$ and the alkene-iodine pi-complex are involved:

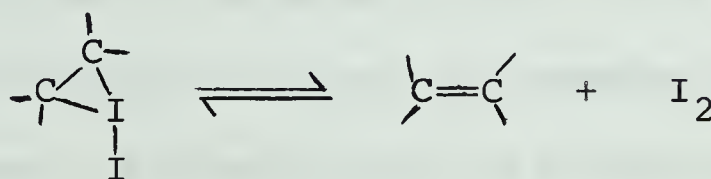


However, the formation of such a highly ordered transition state as would be required in the above mechanism would be unfavorable from an entropy viewpoint. Since iodine may exist in linear chains or other polyatomic species (169), the exact nature of the attacking species or of the entity capturing a split-off iodine atom might vary with iodine concentration.

All of the mechanisms considered above involve reversible reaction steps: according to the principle of microscopic reversibility, the same transition states and intermediates must be involved in the reverse reaction as in the forward reaction. For example, the reverse of the mechanism last considered above becomes:



The pi-complex intermediate may then separate into free iodine and alkene:



We have confirmed that the rate of addition of iodine to cyclohexene in inert, non-polar solvents is accelerated by illumination with

visible light. This effect was especially conspicuous under conditions of low concentrations of reactants and high light intensity; thus, the time required to reach equilibrium could be reduced from a period of days to a period of minutes by illumination of the reaction solution with an ordinary 200-watt light bulb. Evidently, the absorption of visible light by iodine results in the generation of iodine atoms; the iodine atoms must then undergo reaction with alkene via one of the mechanisms postulated above. The decomposition of cyclohexene diiodide to iodine and cyclohexene was also found to be catalyzed by either ultraviolet or visible light. Ultraviolet light could give rise to atomic iodine by homolysis of a carbon-iodine bond while visible light would cause homolysis of any iodine molecules which are present (due to incomplete removal of iodine or to thermal decomposition of the unstable vicinal diiodide).

In the above studies, homolytic reaction was initiated by light. Evidence has recently accumulated, however, for the occurrence of certain spontaneous homolytic reactions which require no external initiator. Poutsma (39-42) has obtained evidence that the addition of chlorine to alkenes in inert, non-polar solvents, in the absence of free radical inhibitors or initiators, occurs via competing homolytic and heterolytic processes. Bartlett et al (6, 26) in their study of the addition of iodine to styrene in solution in carbon tetrachloride in the dark, concluded that two mechanisms were in operation: one process could be

inhibited by oxygen and this was considered to involve a chain reaction initiated by an intermolecular "molecule-induced homolysis" of iodine by styrene; the second mechanism in operation was assumed to be of an ionic nature.

Solvents that have not been degassed may contain relatively large amounts of dissolved oxygen (170), for example, carbon tetrachloride saturated with oxygen is greater than 0.010 M in oxygen (171). The effect of undegassed solvent on the rate of addition of iodine to cyclohexene was found to be quite striking. For example, for an undegassed solution, initially, 0.05 M in both iodine and cyclohexene, reaction was found to have proceeded 27% of the way to equilibrium after 1.5 hours in the dark; for a degassed solution of the same initial concentrations of reactants, reaction was found to have proceeded 89% of the way to equilibrium after the same length of time in the dark. The same equilibrium point was attained in both reactions.

In another experiment, carried out in cyclohexane, with iodine 0.004 M and cyclohexene 0.193 M, an undegassed portion after 2 hours in the dark at 25° had reacted to an extent of only 0.5% (after 20 hours to an extent of 6.5%) whereas a portion, degassed, but kept in the dark at 25° for 1.5 hours, reacted to the extent of 71%. Another portion of the reaction solution illuminated at 25° for three minutes was found to have reacted to the extent of 88.5%.

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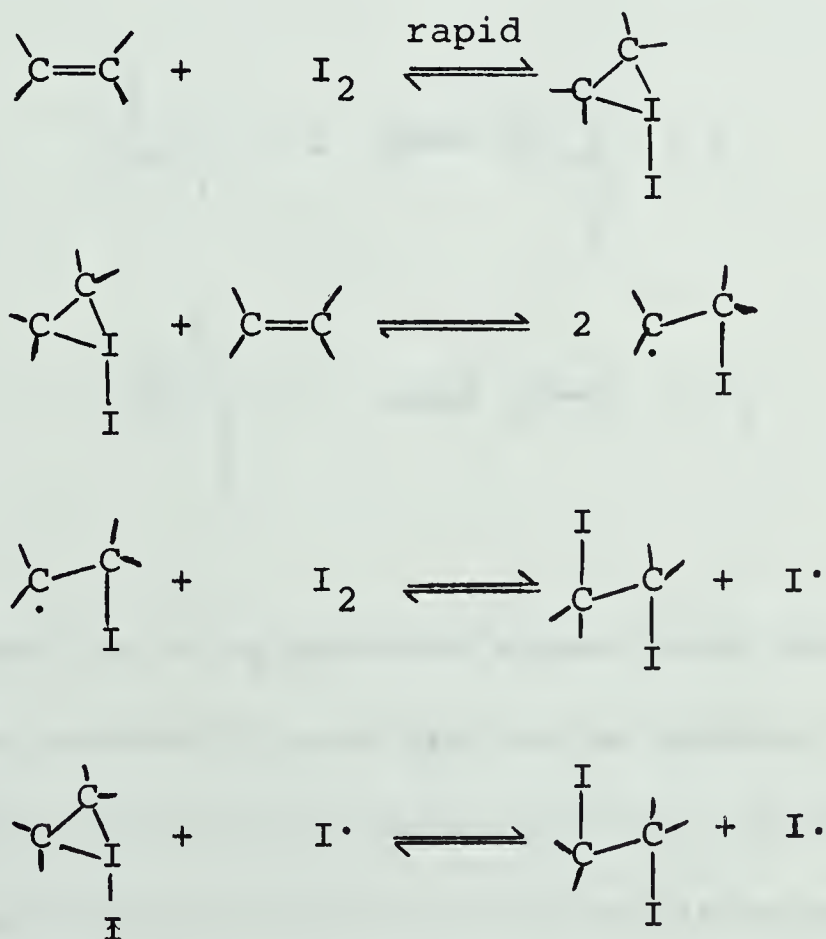
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Removal of oxygen, therefore, allows the addition of iodine to cyclohexene to proceed at a much greater rate. Hence, it must be concluded that a homolytic process, which can be inhibited by oxygen, occurs either exclusively or in competition with other addition processes.

Both Bartlett et al (6, 26) and Poutsma(39, 40) obtained evidence that the spontaneous homolytic halogen-alkene additions were higher order in alkene than in halogen. Poutsma proposes that an initial complex between chlorine and alkene forms and then undergoes further reaction with a second alkene molecule to give two chloroalkyl radicals.

For spontaneous iodine-alkene addition, the following mechanism may be postulated.



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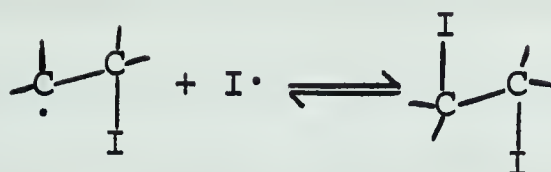
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$$f(x) = \frac{1}{x^2}$$

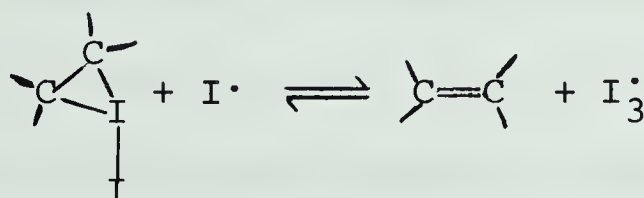
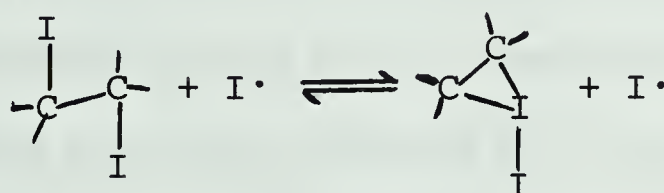
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$$f(x) = \frac{1}{x^2}$$



The above spontaneous homolysis process is represented as a reversible one; however, the reverse reaction would require the coupling of two iodoalkyl radicals, a process statistically unfavorable. Other homolytic deiodination mechanisms would be more probable, for example:



We have been discussing homolytic alkene-iodine addition mechanisms. The catalytic effect of light and the inhibitory effect of oxygen demonstrate the occurrence of such a process. However, the occurrence of a free radical process does not eliminate the possibility that a competing heterolytic process may also be operating.

Evidence for Heterolytic Cyclohexene-Iodine
Addition in Inert Non-polar Solvents

When reactants are uncharged molecules and when the reaction must proceed via a polarized transition state, non-polar solvents would not be expected to be ^{as} favorable for the reaction as polar solvents. For at least two reasons, however, the possibility of heterolytic, alkene-iodine addition in non-polar solvents cannot be ruled out.*

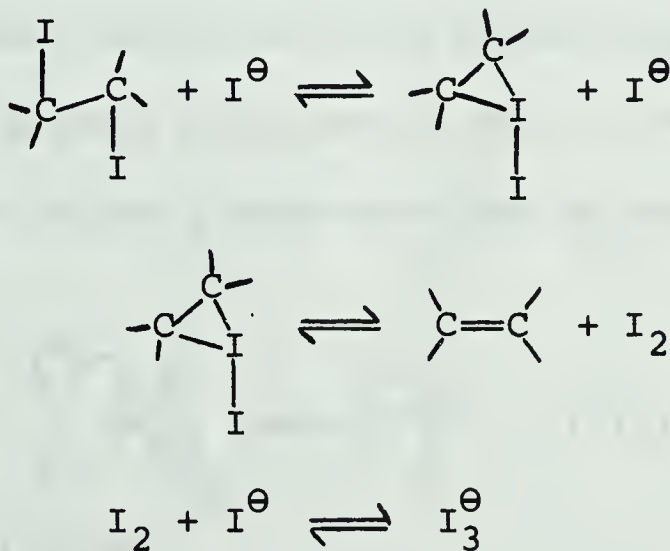
Firstly, iodine molecules are readily polarizable molecules and, therefore, participation of several iodine molecules in the transition state could considerably lower the energy of activation. Indeed, the complex kinetics reported in the iodination studies by Robertson et al (17) and by Bhattacharyya et al (22) were attributed to such a participation.

Secondly, the addition process could, conceivably, involve not only the uncharged alkene and iodine molecules but, also, catalytic amounts of iodide ion. In this way, a polarized transition state could be more readily achieved than in the absence of any ionic reactant. Iodide ion has been shown to effect the elimination of iodine from ethylene diiodide in hydroxylic solvents (1); our investigations, to be discussed later, disclosed that iodide ion also effectively deiodinates alkene diiodides in inert, non-polar solvents. Since iodide ion can be involved in the

*Note added in proof: See C. S. Chad, R. R. Lii, L. C. Chad, and H. M. Chen. Hua Hsueh, 95 (1965) for a paper entitled: 'Solvent effects on the polar addition reaction of iodine to cyclohexene, kinetic study in the various solvents, relation of reaction rate constants to chemical structure and dielectric constants of the solvents.'; Chem. Titles, No. 8 (1966).

deiodination process, then, according to the principle of microscopic reversibility, it can also be involved in the addition process. The existence of a pathway involving iodide ion does not, of course, preclude other pathways for this readily reversible reaction.

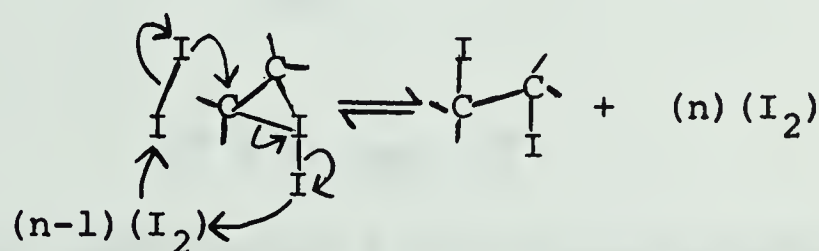
Only one mechanistic study of iodide ion-catalyzed deiodination of alkene diiodide has been reported in the literature; Iredale and Stephan (1) found that the deiodination of ethylene diiodide by equimolar quantities of potassium iodide in ethanol-water was first order in each reactant. On this basis, Hine and Brader (25) have formulated the following deiodination mechanism.



The intermediate iodine-alkene complex was believed to form in a slow rate-determining step and then rapidly decompose to alkene and iodine. Since the reaction was found to be first order in iodide ion (1), Iredale and Stephan concluded that triiodide ion was not a catalyst for deiodination.

The intermediate iodine-alkene complex formulated by Hine and Brader is the same species as we postulated above in our discussion of homolytic addition processes. In the deiodination reaction which involved large concentrations of iodide ion, Hine and Brader viewed the complex as being a very short-lived species. In iodine-alkene additions, especially those occurring in inert, non-polar solvents, and in the absence of appreciable concentrations of iodide ion, the alkene-iodine complex, previously mentioned in our discussion of homolytic processes, appears to be a less transient species. In the forward addition process, we postulated that whether the overall process be homolytic or heterolytic, the initial intermediate in inert, non-polar solvents may be the same, namely, the alkene-iodine complex we have earlier discussed.

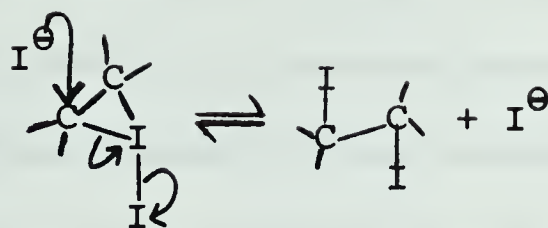
If a heterolytic process exists and if it were to involve iodine but no iodide ion, then, the following mechanism may be conceived.



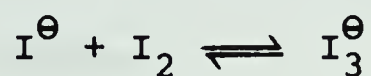
The efficient operation of this mechanism would be expected to require relatively large concentrations of iodine.

If a heterolytic, alkene-iodine, addition process exists and if it were to involve iodide ion as a catalyst, then the following mechanism

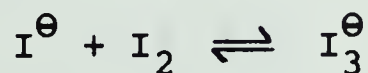
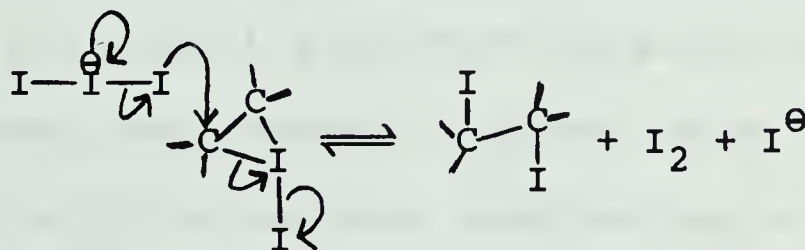
may be conceived.



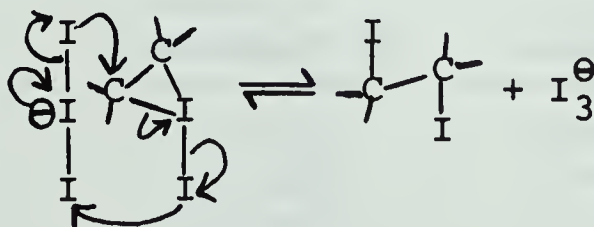
However, iodide ion, present only in trace amounts, in the presence of relatively much greater concentrations of iodine, would be expected to exist largely in the form of triiodide ion:



Although triiodide ion would be expected to be a less nucleophilic species than iodide ion, it is conceivable that it could act as a catalyst:



Except for entropy considerations, a cyclic concerted process involving attack by triiodide ion on the alkene-iodine complex would be attractive:



If triiodide ion catalyzes the addition reaction it would be expected also to catalyze the deiodination reaction. Although Iredale and Stephan (1) did not note any triiodide catalysis in the deiodination of ethylene diiodide, they were employing relatively large concentrations of iodide ion and if iodide ion is a much more effective catalyst than triiodide ion, then, their experiments do not warrant the dismissal of triiodide ion catalysis. It must, also, be kept in mind that Iredale and Stephan employed a polar, hydroxylic solvent; in inert, non-polar solvents, the situation could be much different.

If, in the addition of iodine to cyclohexene, a heterolytic process occurs, it should be subject to effects of solvent polarity. Hence, we measured the rates of addition in various, undegassed solvents in the dark. The rates of approach to equilibrium are plotted in Fig. 18 and the solvents employed, their dielectric constants, and the time, $t_{1/2}$, required in each case for the reaction to reach half-way to its equilibrium point are given in Table IX.

TABLE IX

Effect of dielectric constant of solvent on rate of iodine-cyclohexene reaction.
Temperature 25.0°. Each reactant initially 0.050 M.
Reaction in dark in undegassed solvent.

Solvent	Dielectric constant(172)	$t_{1/2}$, minutes	$k_2(x 10^4)$, l/mole/sec
Carbon Tetrachloride	2.2 (20°)	265	9.7
Benzene	2.3 (20°)	180	6.4
Methylene chloride	9.1 (20°)	15	112
Nitrobenzene	34.8 (20°)	very small	very large

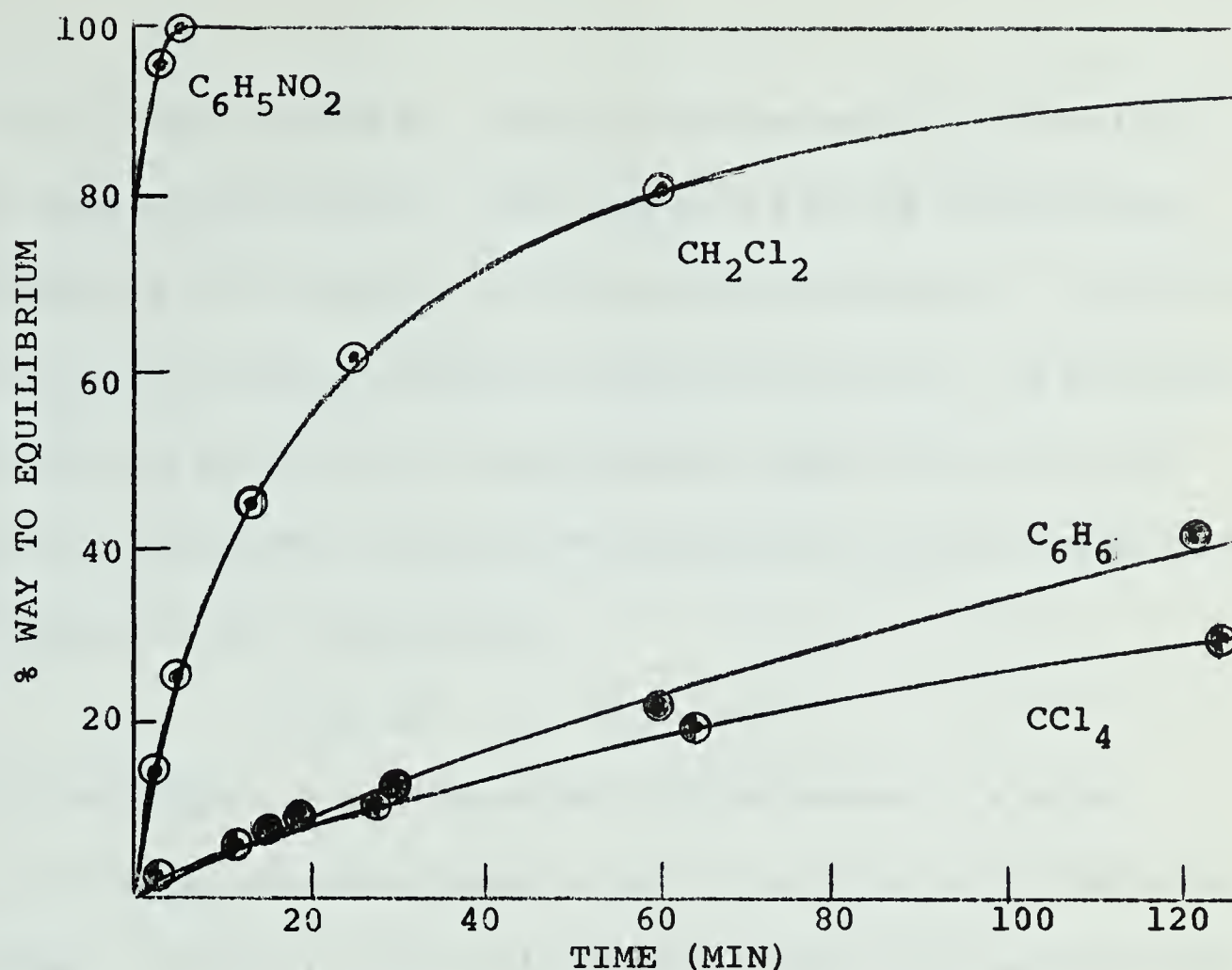


FIG. 18. Approach to equilibrium position with time for cyclohexene-iodine addition in dark in four different solvents (undegassed) at 25° , reactants, 0.050 M.

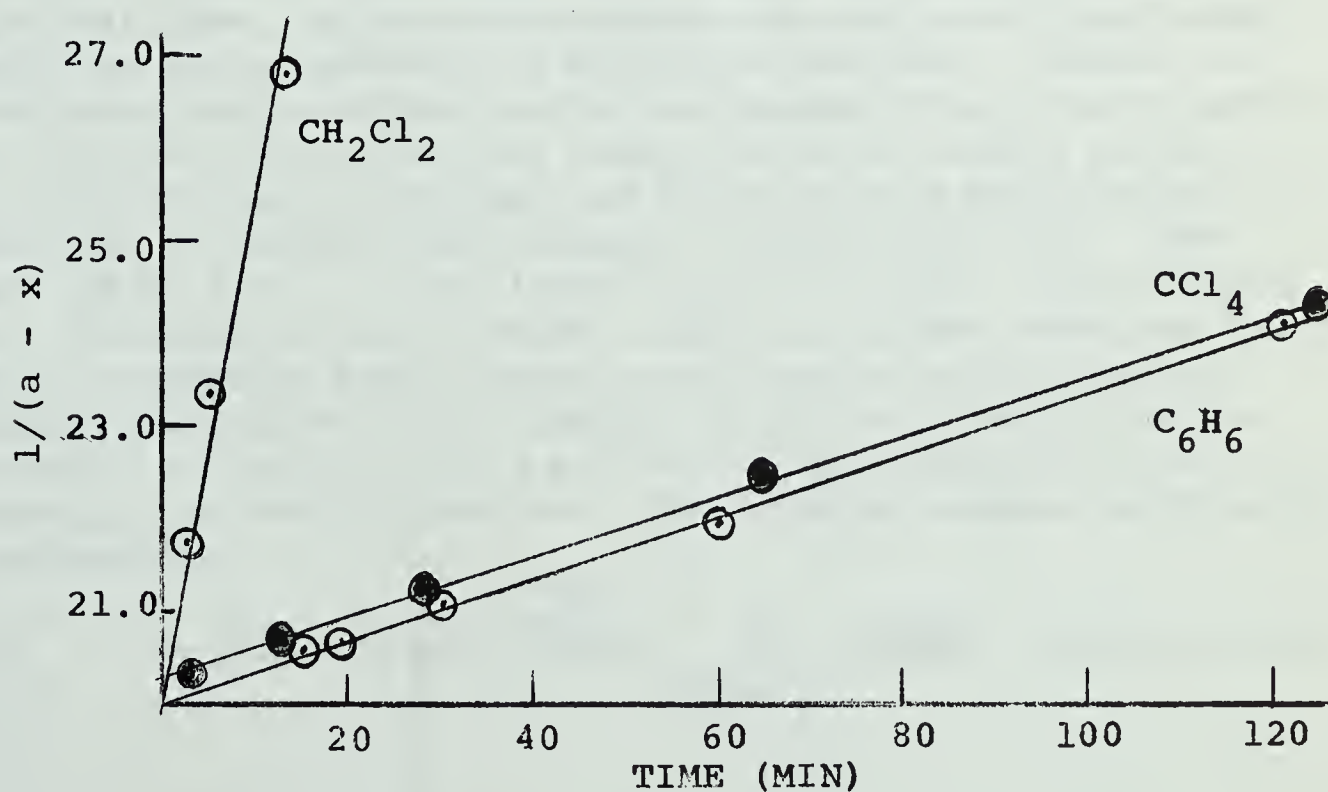


FIG. 19. Plot of second-order rate equation for cyclohexene-iodine addition in dark in three different solvents (undegassed) at 25° , reactants, 0.050 M.

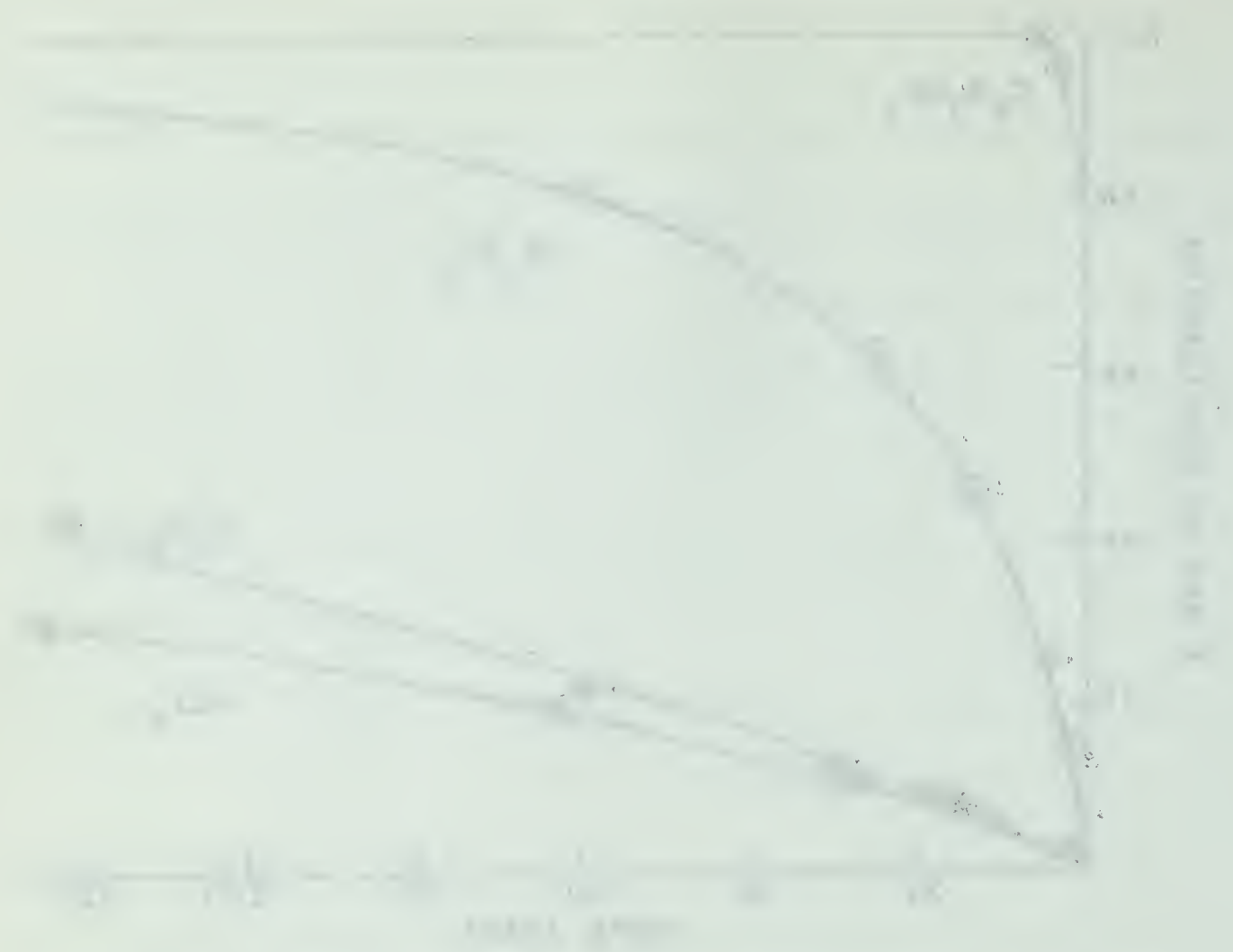


Fig. 1. Relationship between time and variable for three different cases. The curves are labeled 1, 2, and 3. The y-axis is labeled 'TIME, MIN' and the x-axis is labeled 'VARIABLE'.



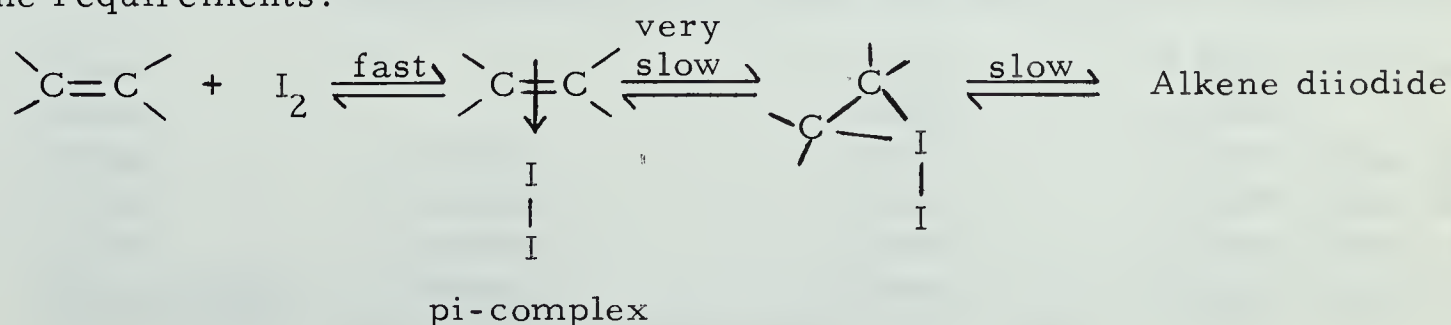
Fig. 2. Relationship between time and variable for two different cases. The curves are labeled 1 and 2. The y-axis is labeled 'TIME, MIN' and the x-axis is labeled 'VARIABLE'.

These measurements did, indeed, show the rate of reaction to be dependent upon solvent polarity; hence, there is a strong indication that ionic processes are available for cyclohexene-iodine addition. Furthermore, in the cases of the solvents, benzene, carbon tetrachloride, and methylene chloride, the data obtained for reactant concentrations during the initial stages of the reaction with less than 30% conversion to products were found to fit the second-order rate equation,

$$1/(a - x) = k_2 t - 1/a$$

where a is the initial concentration of each of the reactants, x is the concentration of cyclohexene diiodide at time t , and k_2 is the second-order rate constant. In Fig. 19, $1/(a - x)$ is plotted versus t for each case and from the slope of the plot a value for k_2 obtained (Table IX).*

*Kinetic investigations were not further pursued. However, if as indicated, cyclohexene-iodine addition proceeds via an over-all second-order process, then, the rate-determining step must have a first-order dependence on the concentration of each of the reactants. Above, we have mentioned the possibility that the intermediate involved in the addition process could be identical with the weakly bonded association product known to form between cyclohexene and iodine which is described as a pi-complex or as an electron donor-acceptor complex (162-168). (See Y. Ogata and K. Aoki. J. Org. Chem. 31, 1625 (1966)). This complex, however, appears to form very readily and to be a rather stable species. In order to accommodate both a second-order reaction and pi-complex formation, a mechanism for diiodide formation must either exclude the pi-complex or include it in such a way that its formation is not rate-determining in the over-all reaction. The following scheme would satisfy the requirements.



In inert, non-polar solvents such as carbon tetrachloride if photolytic and homolytic processes are effectively excluded or inhibited, then, the occurrence of alkene diiodide formation must be via heterolytic processes. We have not made an extensive study of the kinetics of alkene-iodine addition but we did find that at high concentrations of iodine, the addition reaction between iodine and cyclohexene proceeded extremely rapidly which may be taken as an indication that several molecules of iodine may be involved in the rate-determining step.

As mentioned previously, heterolytic, alkene-iodine addition may, conceivably, involve iodide or triiodide ion as a catalyst. We investigated, therefore, the effect on the initial rate of cyclohexene-iodine addition of small amounts of tetra-n-butylammonium iodide. The results are given in Table X and the rates plotted in Figures 20 and 21.

TABLE X

Effect of tetra-n-butylammonium iodide and perchlorate on rate of cyclohexene-iodine addition in dark at 25°, each reactant, 0.050 M Undegassed solvent (carbon tetrachloride:methylene chloride = 4:1) Reaction solution, 10.0 ml, quenched in 10.0 ml 0.100 N thiosulfate

Salt	(Salt), moles/liter	(Cyclohexene diiodide) after 5 min, moles/liter	(Cyclohexene diiodide) at equilibrium, moles/liter
None		0.0014	0.0290 (after 48 hours)
None		0.0014	0.0290*
Iodide	0.000225	0.0033	0.0290 (after 48 hours)
Iodide	0.000450	0.0051	0.0290 (after 48 hours)
Iodide	0.000450	0.0050	0.0280 (after 14 hours)
Perchlorate	0.000450	0.0044	0.0285 (after 50 hours)

*Found after reaction solution illuminated for 10 min. at 25°

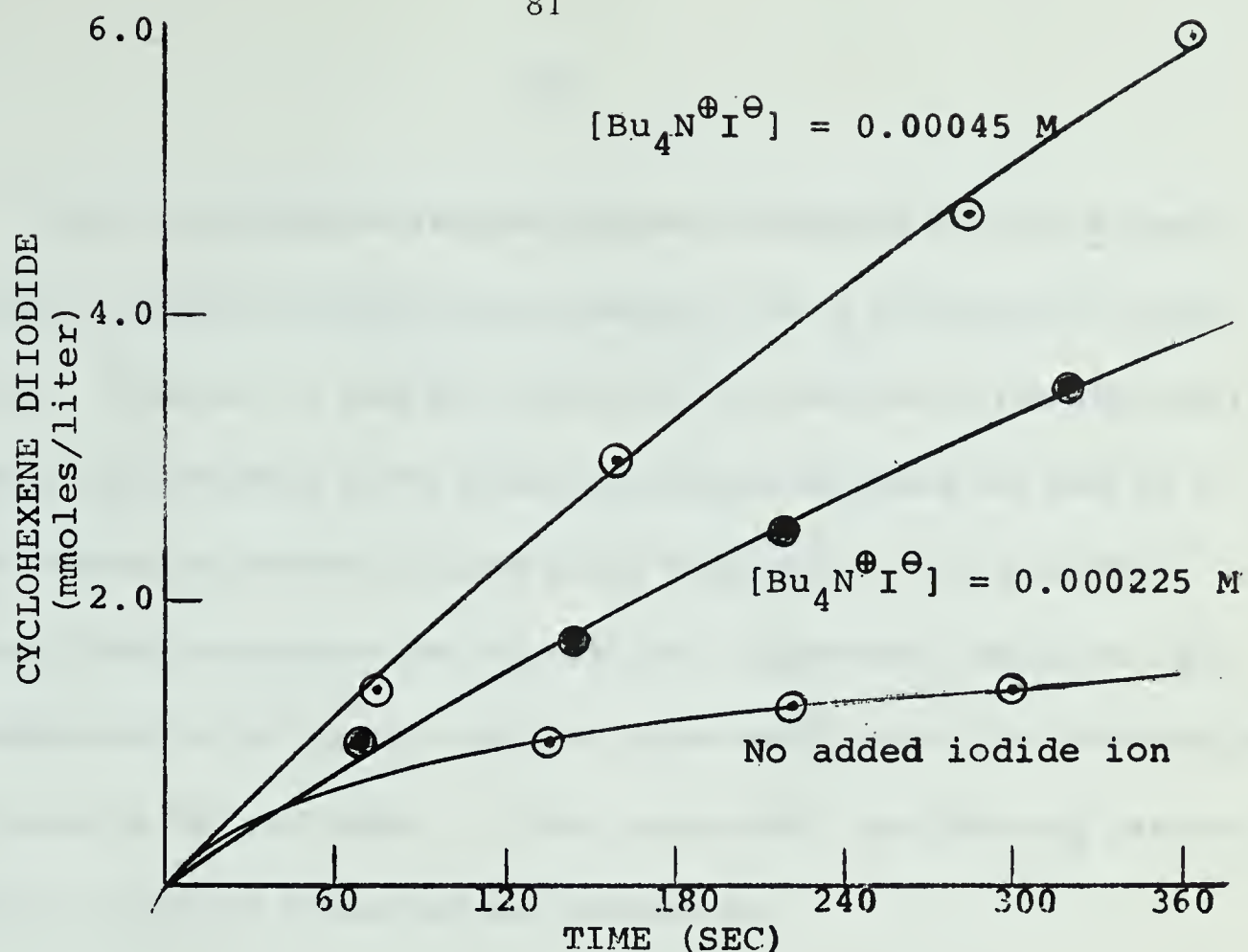


FIG. 20. Effect of iodide ion on rate of cyclohexene-iodine addition in dark at 25°, reactants, 0.050 M in undegassed solvent ($\text{CCl}_4 : \text{CH}_2\text{Cl}_2 :: 4 : 1$).

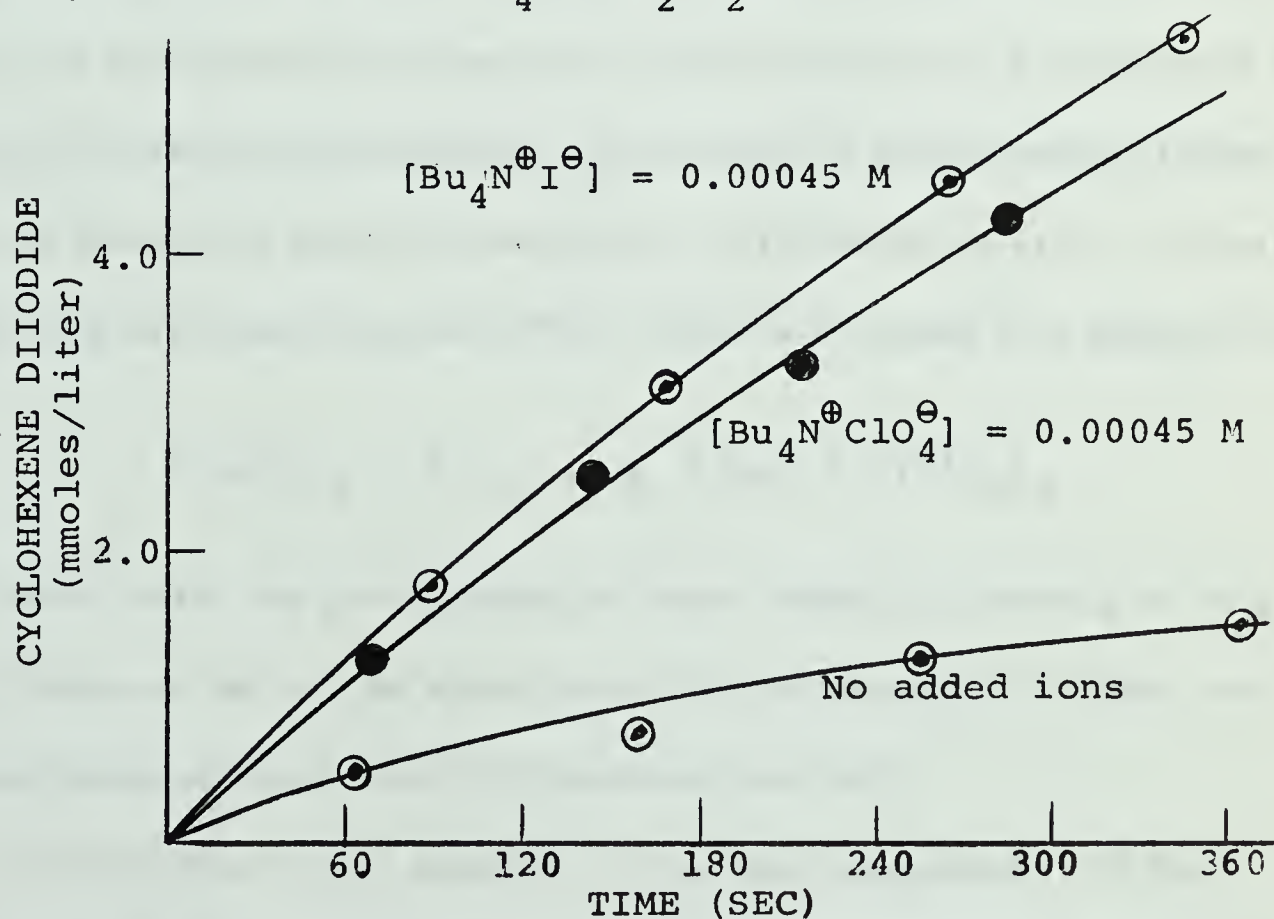


FIG. 21. Effect of iodide ion and of perchlorate ion on rate of cyclohexene-iodine addition in dark at 25°, reactants, 0.050 M in undegassed solvent ($\text{CCl}_4 : \text{CH}_2\text{Cl}_2 :: 4 : 1$).

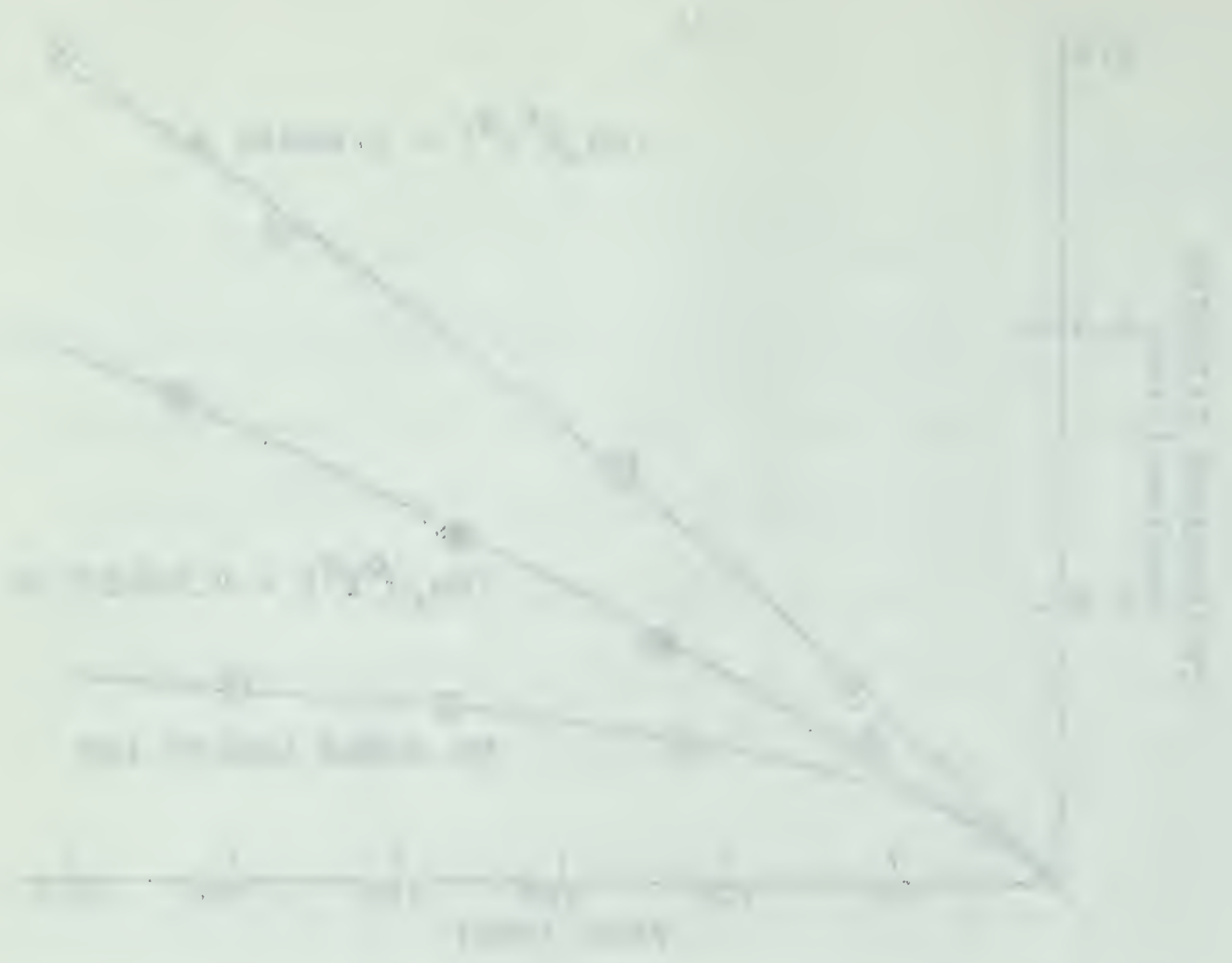


Fig. 1. Rate of reaction vs. concentration of reactants. The curves show that the rate of reaction increases with the concentration of reactants, and that the rate of reaction is highest for the reaction with the highest order.



Fig. 2. Rate of reaction vs. concentration of reactants. The curves show that the rate of reaction increases with the concentration of reactants, and that the rate of reaction is highest for the reaction with the highest order.

These results demonstrate that small amounts of tetra-n-butylammonium iodide do definitely increase the rate of cyclohexene-iodine addition. However, it was also found that the addition of tetra-n-butylammonium perchlorate to the reaction mixture enhanced the rate to a similar extent, as shown in Table X and Figure 21. It is possible, however, that perchlorate ion, in some way, generates iodide ion, and that iodide ion is the specific catalyst, even when tetra-n-butylammonium perchlorate is the salt added. Thus conceivably, the following reaction could occur between iodine and perchlorate ion.



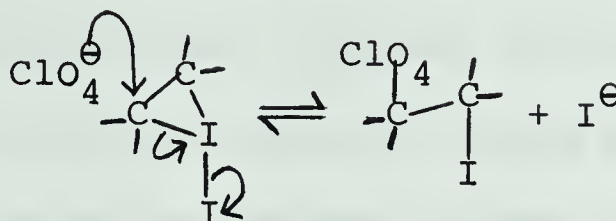
Indeed, we found that the ultraviolet-visible spectrum of a solution of iodine and tetra-n-butylammonium perchlorate in carbon tetrachloride exhibited absorption bands characteristic of triiodide ion (173). Silver perchlorate has been reported (174) to react with iodine in a similar way:



In the latter case, the precipitation of silver iodide is a strong driving force; however, as will be shown later, the formation of triiodide ion can be a strong driving force for reactions, as well.

In non-polar, inert solvents, it has been suggested (175) that perchlorate ion may be capable of forming stable perchlorate esters.

If this should occur in our case, iodide ion would be produced:



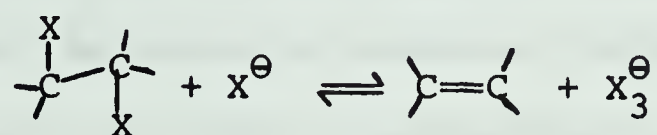
Although it is difficult to establish whether iodide ion is a specific catalyst, at least, the demonstrated effect of added ionic species substantiates that cyclohexene-iodine addition may occur via a heterolytic path.

Reaction of Alkene Diiodides with Halide Ion

Only two reactions of alkene diiodides with halide ion appear to have been reported and, in both cases, the reactions have involved ethylene diiodide as substrate. The better known of these reactions is that of ethylene diiodide with potassium iodide in ethanol-water to give ethylene and triiodide ion (1, 25). The other reaction, reported about one century ago (176) involved the reaction of ethylene diiodide with mercuric chloride to give ethylene chloriodide. The mechanism of this reaction has not been elucidated but the possibility arises that ethylene chloriodide could have formed in either of two ways: (i) by substitution or, (ii) by deiodination followed by addition of iodine monochloride to ethylene.

Except for their dehalogenation by iodide ion, (25, 88, 177-184)

other alkene dihalides have likewise received little study with regard to their reactions with halide ion. The fact, however, that alkenes react with tribromide ion to give alkene dibromides and bromide ion (51, 54) suggests that reactions of halide ions with alkene dihalides are reversible reactions of the type represented by the following equilibrium equation.



When $\text{X} = \text{I}$, the equilibrium must lie to the right, whereas when $\text{X} = \text{Br}$, the equilibrium must lie to the left, or, by employing the proper reaction conditions, may be shifted in these directions. Thus, dehalogenation of alkene dihalides by iodide ion is usually effected by the use of about a ten-fold excess of iodide ion (178-182). The ability of iodide ion to dehalogenate alkene dihalides appears to decrease, approximately, according to the following order of alkene dihalides (25, 177, 180, 183): diiodide, bromoiodide, bromochloride, dibromide, dichloride. Possibly, this trend is due to equilibrium factors. Equilibria between alkene dihalide and halide ion, on one side, and alkene and trihalide ion, on the other side, do not seem to have received general consideration, much less, thorough study.

We have investigated the reactions of cyclohexene diiodide with halide ions. Since cyclohexene diiodide had to be prepared in inert

solvents, we had to choose salts that would be soluble in the chosen solvents. Accordingly, we used methylene chloride and chloroform as solvents and tetraalkylammonium halides as sources of halide ions. Prior to our work, reactions of alkene dihalides with tetraalkylammonium halides do not appear to have been investigated. In aprotic solvents, halide ions are poorly solvated and, therefore, are excellent nucleophiles (185). Furthermore, the larger the halide ion, the better it can bear a negative charge; hence, the order of nucleophilicity in aprotic solvents decreases in the order, chloride ion, bromide ion, iodide ion, which is the opposite order to that found in protic solvents (185).

We found that colorless solutions of cyclohexene diiodide rapidly eliminated iodine upon addition of tetraalkylammonium iodide, bromide, or chloride. An investigation of the reaction of cyclohexene diiodide (present in an equilibrium solution with iodine and cyclohexene) with a ten-fold excess of halide ion showed by iodometric analysis that, after about five minutes under the conditions employed, the deiodination reaction was 100% complete in the case of iodide ion, about 98-99% complete in the case of bromide ion, and about 95% complete in the case of chloride ion.

Although iodide ion has often been found to dehalogenate alkene dihalides, bromide ion or chloride ion do not appear to have been previously reported to do so (186). Ethylene diiodide has frequently been reported

to be subject to nucleophilic attack at iodine rather than at carbon (25); since we have performed our reactions under conditions where chloride ion and bromide ion are expected to be superb nucleophiles (185), the occurrence of deiodination is not surprising.

The above reaction of cyclohexene diiodide with excess chloride ion to give cyclohexene was followed by a second reaction which, after one day, gave cyclohexene trans-chloroiodide in a yield of nearly 75%. In a second experiment, cyclohexene trans-chloroiodide was prepared preparatively by this method; its n.m.r. spectrum (Fig. 22) was identical to that previously published by Premuzic and Reeves (137).

In the reaction of cyclohexene diiodide with excess bromide ion, cyclohexene bromoiodide was not isolated but iodometric analysis indicated the possibility that, after one day, it had formed to the extent of less than 5%. As shown later, cyclohexene bromoiodide is much less stable than cyclohexene chloroiodide; in the presence of a large excess of halide ion, its extensive formation is, therefore, improbable.

In order to establish the relative stabilities of cyclohexene diiodide, cyclohexene bromoiodide, and cyclohexene chloroiodide, in the presence of an equimolar amount of tetraalkylammonium iodide, the positions of equilibrium for the following reversible reactions were measured.

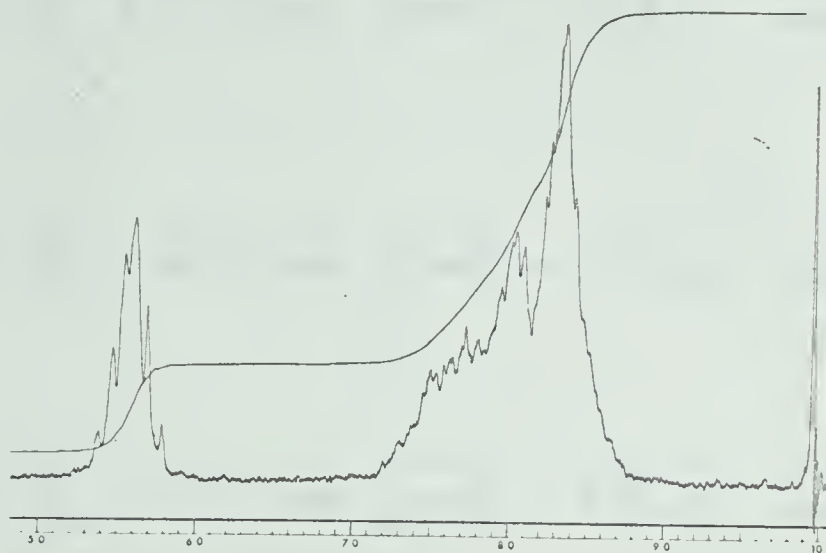


FIG. 22. N.m.r. spectrum (60 Mc.p.s.) of cyclohexene trans-chloriodide, about 50% solution in carbon tetrachloride.

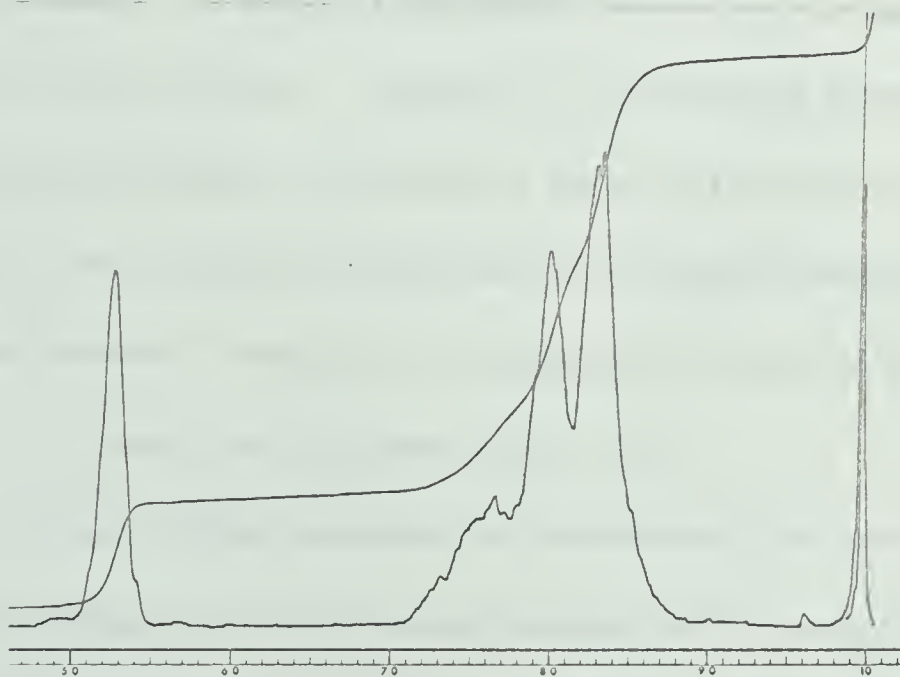
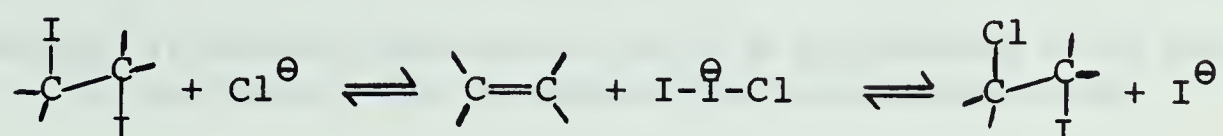
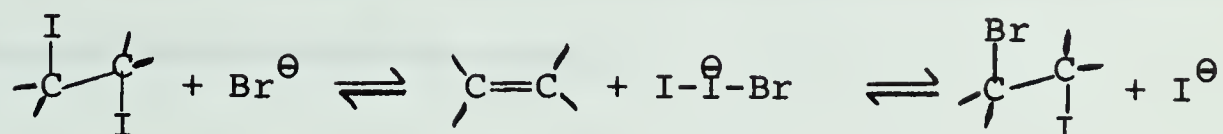
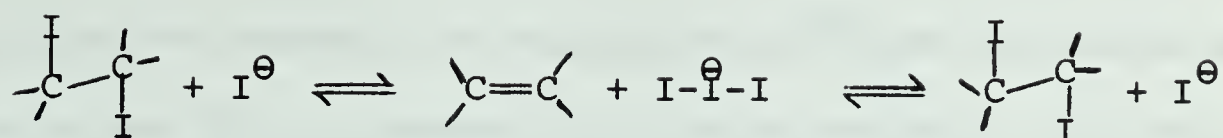


FIG. 23. N.m.r. spectrum (60 Mc.p.s.) of cyclohexene trans-bromiodide.



The reactions between cyclohexene and equimolar amounts of triiodide ion, diiodobromide ion, and diiodochloride ion at high concentration (1.25 M) in chloroform, at equilibrium, were analyzed by n.m.r. spectroscopy. In none of the three reactions was any cyclohexene diiodide found to form. However, cyclohexene bromoiodide and cyclohexene chloroiodide were found to form to the extents of about 13.7 and 43.5%, in the respective reactions involving diiodobromide and diiodochloride ion. (An authentic sample of cyclohexene bromoiodide was prepared and its n.m.r. spectrum is given in Fig. 23).

In more dilute solution in chloroform the same reactions, as well as the reactions of cyclohexene diiodide with iodide, bromide, and chloride ion, and the reaction of cyclohexene chloroiodide with iodide ion, were investigated iodometrically (equimolar amounts of reactants being used in all cases). The results of all these reactions are presented in Table XI.

The equilibrium position in the reaction of $\text{I}_2\text{Cl}^\ominus$ with cyclohexene is seen to be near 50% cyclohexene chloroiodide formation, while that for the reaction of $\text{I}_2\text{Br}^\ominus$ with cyclohexene is only about 15% towards cyclohexene bromoiodide formation.

TABLE XI

Percentage cyclohexene haloiodide formed at equilibrium in the reactions of cyclohexene with tetraalkylammonium diiodohalides

Reaction	Per cent cyclohexene haloiodide at equilibrium	
	By n.m.r. ^a	By titration ^b
(i) $\text{C}_6\text{H}_{10}\text{I}_2 + \text{Bu}_4\text{N}^\oplus \text{I}^\ominus$	-	0.0
(ii) $\text{C}_6\text{H}_{10} + \text{Bu}_4\text{N}^\oplus \text{I}_3^\ominus$	0.0	0.0
(iii) $\text{C}_6\text{H}_{10}\text{I}_2 + \text{Bu}_4\text{N}^\oplus \text{Br}^\ominus$	-	15.0
(iv) $\text{C}_6\text{H}_{10} + \text{Bu}_4\text{N}^\oplus \text{I}_2\text{Br}^\ominus$	13.7	16.3
(v) $\text{C}_6\text{H}_{10}\text{I}_2 + \text{Et}_4\text{N}^\oplus \text{Cl}^\ominus$	-	52.5
(vi) $\text{C}_6\text{H}_{10} + \text{Et}_4\text{N}^\oplus \text{I}_2\text{Cl}^\ominus$	-	52.5
(vii) $\text{C}_6\text{H}_{10} + \text{Bu}_4\text{N}^\oplus \text{I}_2\text{Cl}^\ominus$	43.5	49.0
(viii) $\text{C}_6\text{H}_{10}\text{ICl} + \text{Bu}_4\text{N}^\oplus \text{I}^\ominus$	-	49.0

^aReactants, in chloroform, 1.25 M; reaction temperature, 25°, but temperature in n.m.r. spectrometer about 38°.

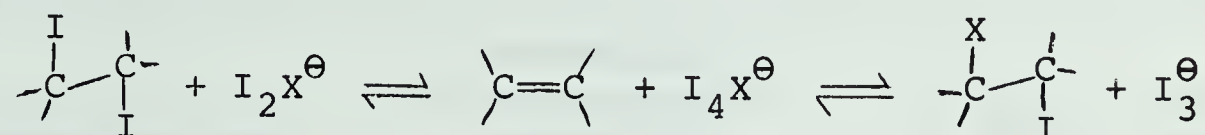
^bReactants, in chloroform, 0.050 M, except for reactions v and vi where the initial solution in chloroform (reactants, 0.050 M) was diluted one-fold with methylene chloride to maintain solution; reaction temperature, 25°.

The order of stability of the above trihalide ions in aprotic solvents does not appear to have been determined (169). However, since the order of nucleophilicity of halide ions in aprotic solvents is $\text{Cl}^{\ominus} > \text{Br}^{\ominus} > \text{I}^{\ominus}$, then, the order of stability of the trihalide ions formed upon reaction with a molecule of iodine might be expected, on this basis, to be $\text{I}_2\text{Cl}^{\ominus} > \text{I}_2\text{Br}^{\ominus} > \text{I}_3^{\ominus}$. Also since the electrophilicity of the halogens, iodine monochloride, iodine monobromide, and iodine, decreases in the order given, then, the order of stability of the trihalide ions formed upon reaction with an iodide ion would again be expected to be the same as that listed above.

If this order of trihalide ion stability is correct, it does not appear that trihalide ion stability is as an important a factor in determining the position of equilibrium in the above reactions as is the stability of the cyclohexene dihalide involved in the same reaction. Since carbon-halogen bond strengths increase in the order (187): carbon-iodine (57 kcal/mole), carbon-bromine (65 kcal/mole), and carbon-chlorine (78 kcal/mole), then, in the above reactions, the formation of the more stable trihalide ion is accompanied by the formation of a more stable cyclohexene dihalide. Thus, if our assumptions are correct, the reason that some reaction occurs between alkene and diiodochloride ion but none between alkene and triiodide ion is not that diiodochloride ion is less stable than triiodide ion but that cyclohexene chloriodide is a much more stable compound than cyclohexene diiodide.

The resulting equilibria when cyclohexene and tetraalkylammonium

halide ion were allowed to react with twice the molar proportion of iodine were also determined by iodometric analysis. The situation may be depicted, as follows, in which the formation of cyclohexene chloroiodide or cyclohexene bromoiodide is accompanied by the formation of triiodide ion.



Titration indicated that cyclohexene chloroiodide formed in 90% yield and that cyclohexene bromoiodide formed in 57% yield. Hence, excess iodine must shift the equilibria to the side of alkene chloroiodide and alkene bromoiodide.

The formation of cyclohexene bromoiodide and triiodide ion in the reaction of cyclohexene with tetraiodobromide ion was substantiated by a comparison of the near ultraviolet spectra of solutions of $\text{I}_4\text{Br}^\ominus$, I_3^\ominus , and $\text{I}_4\text{Br}^\ominus + \text{I}_3^\ominus$, with the spectrum of the reaction solution. The position of absorption maxima and the absorbances of these solutions are given in Table XII. The relatively intense absorption maxima at 362 m μ and at 292 m μ given by the reaction solution (iv) are indicative of the presence of triiodide ion (173); moreover, comparison of the intensities of these absorptions with those for each of the other solutions (i-iii) suggests that triiodide ion must be present in a concentration of about 1.0×10^{-5} M, i.e., the formation of cyclohexene bromoiodide must have proceeded to the extent 75%.

TABLE XII

Absorptions in the near ultraviolet spectra of tetraiodobromide and triiodide ions compared with the absorptions of the equilibrium reaction solution of tetraiodobromide ion with cyclohexene.
Solvent, methylene chloride.

Polyhalide Ion(s)	Concentration of each polyhalide ion, moles/liter	λ_{max} , m μ	Absorbance (1-cm cell)
(i) $\text{I}_4\text{Br}^\ominus$	2.0×10^{-5}	360 282	0.10 0.78
(ii) I_3^\ominus	2.0×10^{-5}	365 295	0.41 0.97
(iii) $\text{I}_4\text{Br}^\ominus + \text{I}_3^\ominus$	$1.0 \times 10^{-5}{}^a$	360 290	0.22 0.82
(iv) $\text{I}_4\text{Br}^\ominus + \text{C}_6\text{H}_{10}$	$2.0 \times 10^{-5}{}^b$	362 292	0.32 0.90

^aTotal concentration of $\text{I}_4\text{Br}^\ominus$ and I_3^\ominus , 2.0×10^{-5} M.

^bInitial concentration of $\text{I}_4\text{Br}^\ominus$, 2.0×10^{-5} M; however, the values listed in the table are for the reaction solution at equilibrium.

Ethylene diiodide, like cyclohexene diiodide, was found to be transformed into alkene chloriodide by reaction with an equimolar amount of diiodochloride ion. Since alkyl-substituted ethylenes are more reactive towards halogens than ethylene, itself, (70-72) it was not unexpected to find that the inclusion of an equimolar quantity of cyclohexene in the above reactions led to cyclohexene chloriodide with little or no ethylene chloriodide. Indeed, even when an equimolar quantity of ethylene was maintained in the reaction between ethylene

diiodide, cyclohexene, and diiodochloride ion, no evidence of ethylene chloriodide formation was found.

Reactions of Alkene Diiodides with Nucleophilic Species Other Than Halide Ion

Introduction. Ethylene diiodide appears to be the only alkene diiodide that has been studied with regard to chemical reaction with nucleophilic reagents. Three possible courses of reaction may be postulated: dehydrohalogenation, dehalogenation, and substitution; all three types of reaction have been reported to occur.

Although Spence (188) claimed a 35% yield of vinyl iodide in the reaction of sodium ethoxide with ethylene diiodide, others (189, 190) report that this reagent leads mainly to ethylene. Nucleophilic attack upon iodine rather than upon carbon or hydrogen appears to be the case with the reagents, thiosulfate, thiophenolate, thiocyanate, and hydroxide ion (189-191) as well as with iodide ion (1, 25); ethylene rather than vinyl iodide or substitution products is formed in all cases. However, substitution products have been reported in the reaction of ethylene diiodide with mercuric nitrate (28), and silver butyrate (28), as well as with mercuric chloride (176).

The latter reactions giving rise to substitution products appear, generally, to have been carried out in the cold in inert, non-polar solvents while the former reactions, giving rise to ethylene, appear to have been

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carried out at higher temperatures and in more polar solvents. Thus, in the cases where no substitution products were found, ethylene was usually distilled from the reaction solution as it formed. In the cases where substitution products were found it was possible that these same products could have been obtained had ethylene been combined with the nucleophilic reagent in the presence of iodine. Indeed, it has been found by Birckenbach and Goubeau (28) that the reaction of mercuric nitrate and iodine with ethylene leads to the same product, 2-iodoethyl nitrate, as the reaction of mercuric nitrate with ethylene diiodide. Thus, in cases where nucleophilic reagents have been reported to lead to substitution products upon reaction with ethylene diiodide, the mechanism of the reaction may very well involve a deiodination process followed by an addition process.

Ethylene diiodide has also been reported to undergo reaction in warm ethanol to give 1-iodo-2-ethoxyethane, the same product being attainable by passage of ethylene into a mixture of iodine and ethanol (192, 193). Again, however, the mechanism of this reaction has not been elucidated.

Reaction with Acetate Ion. The formation of alkene acetoxiodide by the reaction between equimolar amounts of iodine, silver acetate, and alkene is believed to proceed by a mechanism involving the formation of acetyl hypoiodite and its subsequent electrophilic addition to the alkene (194).

Ethylene diiodide has been reported to react with silver butyrate with the formation of ethylene iodobutyrate (28) but the mechanism of the transformation has not been elucidated. We have investigated the reaction of cyclohexene diiodide and ethylene diiodide with acetate ion and conclude that the formation of alkene acetoxyiodide arises predominantly, if not exclusively, via alkene and acetyl hypoiodite.

Tetra-n-butylammonium biacetate as well as silver acetate was found to lead to the formation of alkene acetoxyiodide upon reaction with cyclohexene diiodide or ethylene diiodide. Also, a heterogeneous reaction mixture of equimolar amounts of potassium acetate and cyclohexene with twice the molar proportion of iodine in carbon tetrachloride, shaken for several days, gave cyclohexene trans-acetoxyiodide in 50% yield.

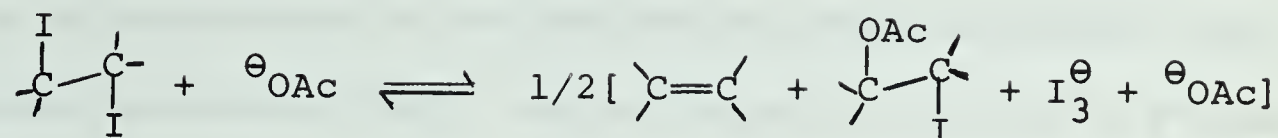
The addition, however, of acetate ion to a colorless solution of cyclohexene diiodide or ethylene diiodide led to an immediate coloration, indicating the liberation of iodine. When a ten-fold excess of tetra-n-butylammonium biacetate was added to cyclohexene diiodide in methylene chloride and the solution immediately iodometrically analyzed it was found that about 90% of the diiodide had undergone elimination. These observations suggested that deiodination of cyclohexene diiodide was a rapid process which must precede formation of alkene acetoxyiodide.

This hypothesis was substantiated by the following experiments.

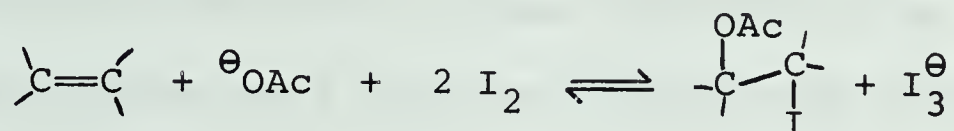
Twice the molar quantity of ethylene diiodide was added to an equimolar mixture of tetra-n-butylammonium biacetate and cyclohexene in solution in methylene chloride. The ethylene diiodide was shown by n.m.r. spectroscopy to react slowly and after four days when the reaction mixture was worked up, the acetoxyiodides of ethylene and cyclohexene were obtained in a ratio of 1:4, respectively. Similarly, addition of silver acetate to a solution of equimolar quantities of ethylene diiodide and cyclohexene in acetic acid and acetic anhydride gave the acetoxyiodides of ethylene and cyclohexene in a ratio of 1:5, respectively. In each of the above experiments, ethylene diiodide must have undergone deiodination with the formation of ethylene and acetyl hypoiodite. Cyclohexene and ethylene would then compete for reaction with acetyl hypoiodite. The formation of cyclohexene acetoxyiodide in quantities much larger than those obtained for ethylene acetoxyiodide may be attributed to the greater reactivity of alkyl-substituted ethylenes over ethylene with regard to electrophilic addition (70-72), as well as to the tendency of gaseous ethylene to escape from the reaction solution.

In the reaction of tetra-n-butylammonium biacetate with alkene diiodides to give alkene acetoxyiodides, iodide ion would be produced so that it was not surprising to find what appeared to be tetra-n-butylammonium triiodide produced in about the same yield as acetoxyiodide. The stoichiometry of this reaction must be that depicted in the following

equation.



The reaction of alkenes with iodine and acetate ion in the absence of a cation such as silver which can effectively remove iodide ion must, therefore, use up a mole of iodine by reaction with iodide ion:

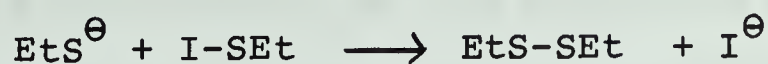
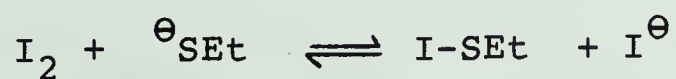


Thus the reaction of equimolar quantities of cyclohexene and tetra-n-butylammonium biacetate with twice the molar quantity of iodine in methylene chloride led to cyclohexene acetoxyiodide in nearly 80% yield.

Reaction with Methoxide Ion. Apparently, the primary reaction of methoxide ion with cyclohexene trans-dibromide (195) is dehydrobromination. Although some dehydroiodination of ethylene diiodide has been reported to occur upon reaction with basic nucleophiles (188), the main reaction appears to be deiodination (189, 190). We found that the reaction of cyclohexene diiodide with sodium methoxide in methanol led to cyclohexene as the only major product.

Reaction with Ethyl Mercaptide Ion. Hine has found that the reaction of thiophenolate ion with ethylene dibromide in methanol leads to bis(phenylthio)ethane (189); similar results are reported by Weygand and Peine on treatment of 1-alkene dibromides with sodium thiophenolate in ether (191). However, treatment of ethylene diiodide with sodium thiophenolate in methanol (189) or in ether (191) has been found to give ethylene. Weygand and Peine (191) found also that dehalogenation rather than substitution occurred when 2-alkene dibromides, (e.g., the dibromides of tetramethylethylene and 2-butene) were treated with sodium thiophenolate; however, the reaction of 2-thiophenoxy-1-chlorocyclohexane with sodium thiophenolate led to 1,2-bis(phenylthio)cyclohexane.

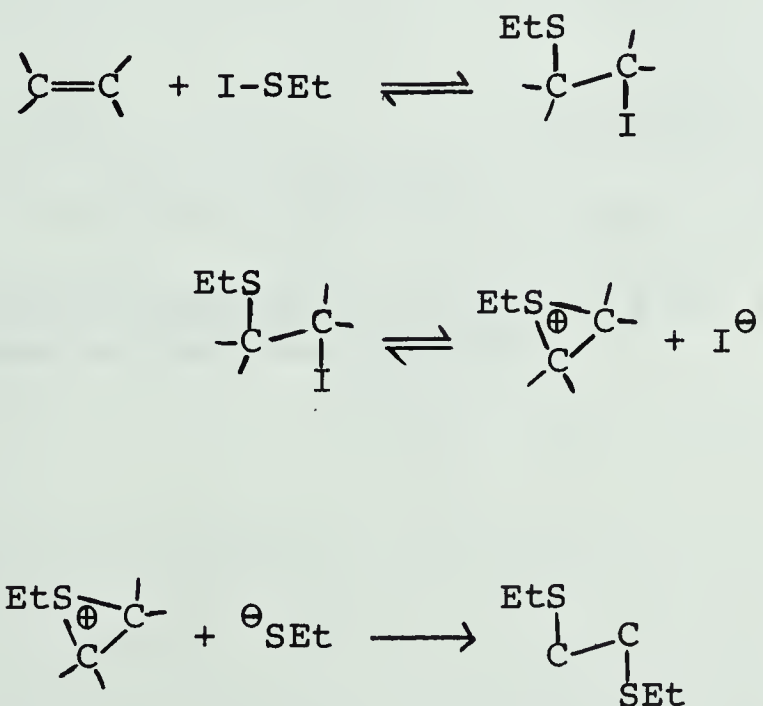
In methanol as solvent, we found that an iodine-cyclohexene-cyclohexene diiodide equilibrium mixture (formed by solution of an equimolar quantity of iodine in cyclohexene) upon reaction with twice the molar quantity of sodium ethyl mercaptide led only to cyclohexene and ethyl disulfide as major products. The latter product which forms readily by reaction between iodine and sodium ethyl mercaptide (196) would produce a high concentration of iodide ion:



Since alcoholic solutions of iodide ion readily deiodinate ethylene diiodide (1, 25), the cyclohexene diiodide in the above reaction may, perhaps, have been deiodinated in this way.

In another experiment cyclohexene diiodide was added to twice the molar amount of solid sodium mercaptide. In this case, a product, the n.m.r. spectrum (Fig. 24) of which corresponded to that expected for 1,2-bis(ethylthio)cyclohexane was obtained (50% yield).

This product may have arisen via substitution or by the following reactions.



The ethyl hypothioiodite (EtSI) would be expected to arise from reaction between iodine and mercaptide ion or from deiodination of cyclohexene diiodide by mercaptide ion. Since the sodium ethyl mercaptide was

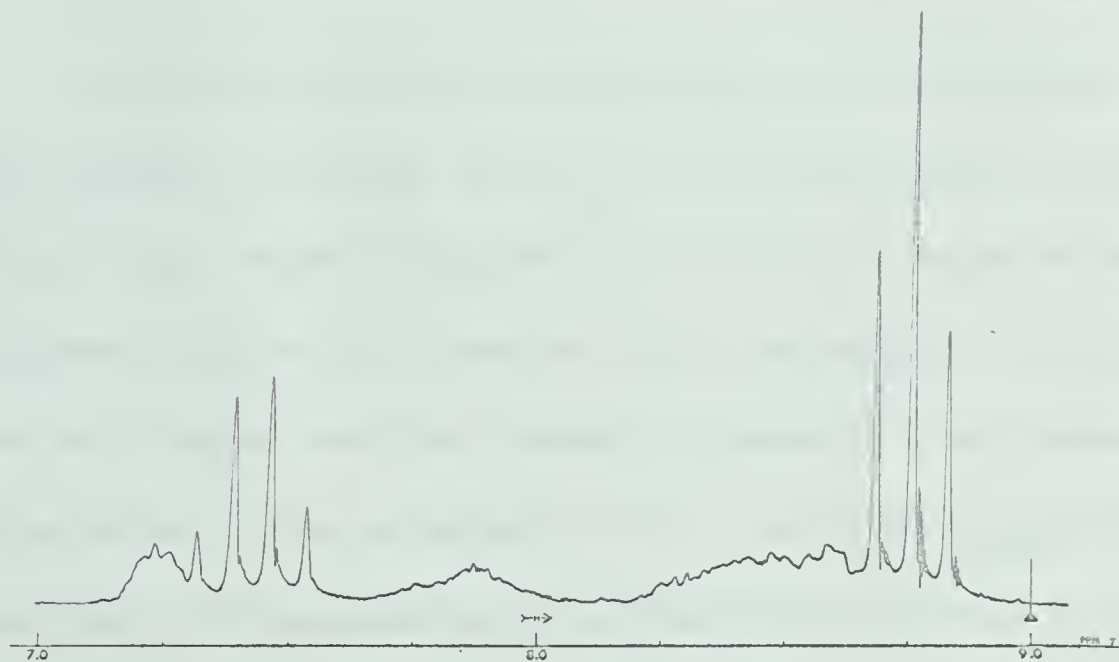


FIG. 24. N.m.r. spectrum (100 Mc.p.s.) of 1,2-bis(ethylthio)cyclohexane in deuteriochloroform.

virtually insoluble in the organic phase, reaction of ethyl hypothiodite could, conceivably, have occurred more rapidly with cyclohexene than with ethyl mercaptide ion.

Concluding Remarks on Reaction of Alkene Diiodides with Nucleophilic Ions

The results of the above investigations of the reactions of cyclohexene diiodide with halide ions, acetate ion, methoxide ion, and ethyl mercaptide ion, show that the most facile route of reaction available to cyclohexene diiodide upon reaction with a nucleophilic ion is deiodination. These deiodination reactions probably proceed by a mechanism which involves attack of the nucleophile, N^{\ominus} , on one of the trans-orientated iodine atoms with elimination of the other iodine atom as an iodide ion. The process could involve a neutral intermediate (25),



which would rapidly decompose to alkene and $I-N$, or it could be entirely concerted, leading directly to iodide ion, alkene, and $I-N$. After iodide ion has been formed, it is entirely possible that it becomes the main deiodination species.

Although deiodination was the primary, most facile reaction of cyclohexene diiodide with the nucleophilic ions studied, secondary reactions

arose in several cases. These subsequent reactions appeared to arise from electrophillic attack of I-N on cyclohexene, followed by attack of N^{\ominus} to give a β -substituted iodocyclohexane.

EXPERIMENTAL

Instrumental

Nuclear magnetic resonance (n.m.r.) spectra at 60 Mc.p.s. were determined with a Varian A60 spectrometer on neat liquids or in the solvents noted in the text. The 100 Mc.p.s. spectrum was recorded on a Varian H.R.100 spectrometer. Chemical shifts are reported in tau (τ) values with tetramethylsilane (TMS) as internal standard.

Ultraviolet and visible spectra were obtained with a Cary model 14 recording spectrometer in the solvents noted in the text.

Gas-liquid chromatography (g.l.c.) was performed with an F and M Model 500 Gas Chromatograph. Unless otherwise noted, a Silicone Oil 200, 4-ft column, commercially supplied with the instrument, was used with helium as carrier gas.

Unless otherwise stated, the source of illumination was a 200-watt, tungsten-filament lamp, which was set at a distance sufficient to avoid heating the reaction solution.

Melting points, which were taken on a heating stage, and boiling points are uncorrected.

Solvents were evaporated on a rotary evaporator, unless otherwise indicated.

Reagents , Solvents , and Standard Solutions

Cycloalkenes , after being refluxed over sodium and distilled, were found to be free of peroxides (197) , as shown by the failure of test samples to bring about the oxidation of iodide ion to iodine (198). However , it was found difficult to retain cycloalkenes peroxide-free for more than a few hours without taking extreme precautions against contact with atmospheric oxygen (197). Moreover , in the case of cyclohexene , trace amounts of 1,3-cyclohexadiene were persistently present as noted by the the presence of an absorption peak at 245 m μ (199) in the ultraviolet spectrum; attempts to remove this impurity by reaction with maleic anhydride (200) proved unsuccessful; heating processes , such as distillation , appeared to increase its concentration (200). Hence , peroxides were removed from cycloalkenes immediately before use by passage of the cycloalkene down a column of activated adsorption alumina (201 , 202). For cyclohexene , ultraviolet spectra showed that this treatment improved its general transmission qualitites but failed to remove the impurity giving rise to the absorption peak at 245 m μ .

Cyclohexane , used as solvent in the determination of ultraviolet spectra of cyclohexene , was purified by treatment with an aqueous , alkaline solution of potassium permanganate; the organic layer was separated , dried , and fractionally distilled , the fraction of b.p. 77-78 $^{\circ}$ at 710 mm pressure being the one retained. Impurities giving rise to

absorption peaks in the ultraviolet spectrum in the region, 215-225 m μ , (with water in the reference cell) were removed by passage of the cyclohexane down a column of activated silica gel (203). In 1-cm cells, with water as reference, cyclohexane, purified in this manner, had an absorbance of about 0.1 at 230 m μ .

Cyclohexene was supplied by Matheson Coleman & Bell, 4-methylcyclohexene by Eastman Organic Chemicals, and cyclopentene, 3-methylcyclohexene, and 4,4-dimethylcyclohexene by Columbia Organic Chemicals; g.l.c. and n.m.r. spectroscopy indicated that these cycloalkenes were greater than 98% pure. The ethylene used was Phillips Research Grade.

The iodine used was Fischer resublimed certified reagent and the iodine monochloride that supplied by Anachemia Chemicals Ltd.. Methylene chloride and chloroform (reagent grades) were passed down columns of adsorption alumina (204) prior to use as solvents. Tetra-n-butylammonium perchlorate (205) and tetra-n-butylammonium bromide (206) were prepared according to the given references. The tetra-n-butylammonium iodide used was that supplied by Eastman Organic Chemicals.

Unless otherwise stated in the text, solutions in organic solvents were dried with anhydrous sodium sulfate.

Standard 0.100 N solutions of sodium thiosulfate were checked against potassium iodate as primary standard and standard 0.100 N solutions of iodine were checked against the standard solution of sodium

thiosulfate (207). When tetraalkylammonium salts were present, a solution of starch was found unsatisfactory as an indicator; the appearance or disappearance of the color due to iodine was taken as the end-point.

Preparation, Purification, and Characterization of Compounds

4-t-Butylcyclohexene. This compound was prepared from 4-t-butylcyclohexanol by way of the 4-t-butylcyclohexyl methanesulfonate according to the procedure of Sicher *et al* (208). The crude product, in pentane, was partially decolorized by passage down a column of adsorption alumina (209). The final product, obtained in 41% yield had a b.p. of 70° at 20 mm pressure and n_D^{20} 1.4595 (for 4-t-butylcyclohexene, reported (209) b.p. 65-66° at 20 mm pressure, reported (208) n_D^{20} 1.4587); on analysis by g.l.c. the material showed a single peak. The n.m.r. spectrum (Fig. 11) of the substance had characteristics in agreement with those expected for 4-t-butylcyclohexene: a broad singlet at τ 4.35, in the region for ethylenic hydrogens, and a narrow singlet at τ 9.13, in the region for methyl hydrogens, with relative intensities of 2:9, respectively.

Ethylene Diiodide. In its simplicity and directness, the following method for the preparation and purification of ethylene diiodide represents an improvement over previously reported methods (1, 12, 210).

Iodine, 127 g (0.50 mole), was suspended in one liter of carbon

tetrachloride and ethylene was bubbled slowly through the mixture as it was stirred at 4° under illumination. After one day most of the iodine had reacted. The slightly purple solution was evaporated at 25° to a brown crystalline residue and the iodine present was removed by sublimation in vacuo. The colorless ethylene diiodide, 134 g (yield, 95%), had m.p. 82.0-83.0° (reported (1) m.p. 82°). Dissolved in chloroform, ethylene diiodide gave an n.m.r. spectrum that consisted only of a narrow singlet at τ 6.33.

A sample of ethylene diiodide, 1.1513 g (4.09 mmoles), m.p. 82.0-82.5° after recrystallization from carbon tetrachloride, was added to a solution of potassium iodide, 5 g (30 mmoles), in 50 ml of water and 150 ml of methanol. After one day the iodine released required 16.2 ml of a 0.50 N aqueous solution of sodium thiosulfate, i.e., 99% of the calculated amount.

The crystalline ethylene diiodide was stored in the dark in a refrigerator to inhibit decomposition. Samples of ethylene diiodide that had become discolored with iodine were purified before use by pumping briefly in vacuo at 25°; although ethylene diiodide also sublimed, it did so at a lower rate.

Cyclohexene Diiodide. Equimolar amounts of iodine and cyclohexene were combined by addition of cyclohexene to a chilled suspension of iodine in carbon tetrachloride; for example, cyclohexene, 2.0 ml (20 mmoles),

the following conditions: (i) the function f is continuous; (ii)

(iii) the function f is bounded; (iv) the function f is measurable;

and (v) the function f is integrable. The first three conditions

are satisfied by the function f in the example given above.

The fourth condition is satisfied by the function f in the example

given above, but the fifth condition is not satisfied by the function

f in the example given above. The function f is not integrable

because it is not bounded. The function f is not measurable

because it is not continuous. The function f is not integrable

because it is not bounded. The function f is not measurable

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was added to iodine, 5.08 g (20 mmoles), in 50 ml of carbon tetrachloride. Under illumination, the mixture was shaken or stirred at 0° for about one hour. In subdued light and at low temperature, near 0° , the faintly violet solution was decolorized by vigorous shaking with an aqueous solution of sodium thiosulfate; the organic layer was separated, dried over anhydrous sodium sulfate and anhydrous sodium thiosulfate, and filtered. In subdued light and at a temperature no greater than 30° , the solution was rapidly evaporated to a syrup.

The n.m.r. spectrum of the light brown syrup (Fig. 3) was found to be identical with that expected for cyclohexene diiodide: the spectrum showed broad peaks centered about τ 7.97 and τ 8.25, in the region for methylenic protons, and a broad singlet at τ 4.95, in the region for protons geminal to halogen (137); integration of peak areas showed the area of the singlet at lower field to be one-quarter the area of the combined peaks at upper field. Initially, there was no evidence in the n.m.r. spectrum for cyclohexene; however, in the warm spectrometer, about $35-40^{\circ}$, the sample soon turned dark brown and a signal near τ 4.38, due to the ethylenic hydrogens of cyclohexene (136), was found to grow slowly in intensity.

Cyclohexene diiodide, freshly prepared as above, was found to form a glass when cooled in a dry ice-acetone bath; however, when the glass was allowed to warm slowly in a salt-ice-water bath, it was found to undergo a crystallization process and on further warming to melt at about -5° .

Cyclohexene *trans*-Chloriodide. A reference sample of this known compound was prepared according to the procedure outlined by Birckenbach and Goubeau (28) which involves the reaction of iodine with a slight excess of cuprous chloride and a large excess of cyclohexene in diethyl ether to give a product, b.p. $110-118^{\circ}$ at 32-38 mm pressure, in greater than 70% yield which has the correct composition for cyclohexene chloriodide. In our preparation the product was purified by slowly distilling it at about 25° and under a pressure of less than 1 mm. The collected syrup was found to decompose when subjected to g.l.c. analysis at temperatures above 100° ; at 100° , however, the decomposition was less than 2% as judged by the ratio of the peaks for cyclohexene chloriodide and cyclohexene, the only peaks observed. The n.m.r. spectrum was identical with that for cyclohexene *trans*-chloriodide published by Premuzic and Reeves (137): the ratio of the intensity of the signals for the methine protons (a multiplet of half-width 15 c.p.s. at τ 5.6) to that of the signals for the methylene protons (a band over the region τ 7.3-8.8) was 1:4.

Cyclohexene *trans*-chloriodide has also been reported (218, 219) prepared by addition of iodine monochloride to cyclohexene in acetic acid to give a product of b.p. $117-118^{\circ}$ at 14 mm pressure. We found that equimolar amounts of iodine monochloride and cyclohexene (in CH_2Cl_2) rapidly underwent reaction to give a product with physical properties identical to those of our reference compound, above. (The n.m.r. spectra of these

preparations were used to identify the reaction product (Fig. 22) resulting from the reaction of iodine, chloride ion, and cyclohexene, as described below).

Cyclohexene *trans*-Bromiodide. Using cuprous bromide, we prepared a reference sample of this compound following the method we used above for preparation of cyclohexene *trans*-chloriodide. Cyclohexene *trans*-bromiodide appears to have been prepared only once before, by Brunel (220), by the reaction of mercuric bromide, iodine, and cyclohexene in diethyl ether to give a rose-colored oil, which boiled with decomposition at 134-136° at a pressure of 28 mm and had a density of 2.07 g/cc at 14°. We purified our product by slow distillation at 50° under a pressure of less than 1 mm. The collected product (density 2.02 g/cc at 25°) was not sufficiently stable for routine analysis by g.l.c.. Even when the temperature was reduced below 100°, broad peaks on the chromatograph indicated a large amount of decomposition. An n.m.r. spectrum of the product (Fig. 23) substantiated its composition to the extent that the ratio of the intensity of the signals for the methine protons (a singlet at τ 5.28, half-width of about 10 c.p.s.) to that of the signals for the methylene hydrogens (a band over the region τ 7.2-8.6) was 1:4.

Tetra-*n*-butylammonium Biacetate. Attempts to prepare tetra-*n*-butylammonium acetate by the addition of an equimolar quantity of silver

acetate to tetra-n-butylammonium bromide or iodide in acetic acid or acetic anhydride resulted in the formation of tetra-n-butylammonium biacetate, a complex, in which one molecule of acetic acid is bound to one molecule of tetra-n-butylammonium acetate. This complex was first characterized by Russel and Anson (214). Preparation of the monoacetate is extremely difficult (215, 216).

The best procedure for the preparation of the biacetate was found to be the addition of an excess of silver acetate to a stirred solution of tetra-n-butylammonium iodide in acetic acid. Precipitated salts were filtered off and the filtrate evaporated, finally, in vacuo; the residual crystalline material, recrystallized from carbon tetrachloride, melted at 116-117° (reported (217) m.p. 116.5-117.5°). In solution in chloroform, the n.m.r. spectrum of this compound (Fig. 25) showed singlets at τ 8.05 and -6.7, for acetoxy protons and acidic protons, respectively, with relative intensities of 6:1, as expected. In addition, the absorption bands characteristic of the tetra-n-butylammonium cation (213) were present: centered about τ 6.65 was an unresolved band due to the α -methylenic protons and from τ 8.0-9.2 there was a broad complex absorption due to the remainder of the protons. The band centered at τ 6.65 had an integrated area 8.0 times that of the signal for the acidic proton at τ -6.7.



FIG. 25. N.m.r. spectrum (60 Mc.p.s.) of tetra-n-butyl-ammonium biacetate in chloroform.

Decomposition of Cyclohexene Diiodide to Cyclohexyl Iodide

On standing at 25° over a period of several days, solutions of iodine in cyclohexene containing one or more moles of iodine per mole of cyclohexene, were found to become viscous mixtures which evolved acidic fumes and deposited black polymer. The n.m.r. spectrum (Fig. 5) of the crude liquid phase showed a multiplet about τ 5.55 and broad peaks at τ 7.95 and τ 8.45; the total area of the upper field peaks was about ten times that of the multiplet at τ 5.55; in fact, the spectrum was found to be identical with that for cyclohexyl iodide (141) (Fig. 6).

Equimolar amounts of iodine and cyclohexene were refluxed in octane for 30 min; the presence of a copious black precipitate and the evolution of acidic fumes indicated that the rate of the decomposition process increased with temperature.

With the injection port at a temperature of 240°, the passage of cyclohexene diiodide through a 4-ft Apiezon M on P column in the gas chromatograph permitted the collection at the column outlet of a dark brown liquid. The n.m.r. spectrum of this substance was identical with that of cyclohexyl iodide. Reinjection into the chromatograph gave a chromatogram containing one sharp peak of retention time identical with that for cyclohexyl iodide.

Spectrophotometric Analysis of Iodine in Cyclohexene-Iodine Addition Reactions

The concentration of iodine in dilute solution in carbon tetrachloride could be determined directly from the intensity of the absorption maximum at 517 m μ in the visible spectrum. By the use of 1-mm cells, iodine concentrations up to about 0.01 M could be measured. The addition of cyclohexene to solutions of iodine in carbon tetrachloride was found to bring about a shift to lower wave lengths of this absorption maximum. Thus, for a solution of iodine and cyclohexene in carbon tetrachloride, when the addition reaction had reached equilibrium and the concentration of cyclohexene, at equilibrium, was about 2.0 M, the absorption maximum was found at 494 m μ ; however, in another solution when the concentration of cyclohexene at equilibrium was about 0.2 M, the absorption maximum for iodine was found at 514 m μ , near its position in the absence of cyclohexene. Hence, for the dilute solutions used below, the absorption maximum in the visible always occurred near 517 m μ .

Spectrophotometric Evidence for the Formation of Cyclohexene Diiodide

A solution about 0.01 M in iodine and about 0.05 M in cyclohexene in carbon tetrachloride as solvent was prepared in the dark and immediately decolorized by shaking vigorously with crystals of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$); the supernatant liquid showed no absorption in the near

ultraviolet.

A solution, initially, 0.0103 M in iodine and 0.050 M in cyclohexene in carbon tetrachloride as solvent was prepared in the dark; immediate examination showed it to absorb strongly in the near ultraviolet, the peak maximum at 302 $m\mu$ having an absorbance of 0.3 when using 1-mm cells. The appearance of this peak, attributed to electron-transfer complexing between iodine and cyclohexene (162-168), was accompanied by a decrease in the intensity of absorbance of iodine at 517 $m\mu$; the concentration of iodine, in fact, decreased to 0.0099 M. On the assumption that the concentration of the complex was 0.0004 M, its extinction coefficient was calculated from the measured absorbance to be 7500.

In carbon tetrachloride as solvent, solutions of either iodine or cyclohexene were shown by their unchanged visible and near ultraviolet spectra to be unaffected upon exposure to illumination from the fluorescent lamps used for lighting the laboratory. However, when a sample of the reaction solution, described in the last paragraph, in a 1-mm quartz cell, was exposed to one of the fluorescent lamps, at a distance of about 6 in for 15 sec, re-examination of the visible and near ultraviolet spectra of the sample showed that the concentration of iodine had decreased about 22% while the intensity of the band in the near ultraviolet had doubled and its maximum had moved to about 282 $m\mu$. Illumination for a further 30 sec brought the total amount of iodine having reacted to about 44%; the band in

the ultraviolet had again increased about two-fold in intensity and its maximum had moved down to 277 $m\mu$. Finally, after a total of about 3 min of illumination, the reaction appeared to have reached equilibrium; about 69% of the iodine had reacted and the band in the ultraviolet spectrum had its maximum at 275 $m\mu$ with an absorbance of 0.6.

The absorption maximum at 275 $m\mu$ was attributed to cyclohexene diiodide (138-140). On the assumption that the concentration of this compound was 0.007 M, its extinction coefficient was calculated to be 850. On the same assumption, the equilibrium constant, K_{Eq} , for cyclohexene-iodine addition was calculated to be 54 liter-mole⁻¹.

The main reaction solution described above was allowed to reach equilibrium under illumination; the iodine still present was removed by the addition of crystals of sodium thiosulfate and vigorous agitation of the mixture. The visible and near ultraviolet spectra of the resulting colorless solution showed only a strong absorption maximum at 275 $m\mu$. However, exposure to fluorescent light for 2 min caused a reappearance of iodine in a concentration of 0.0005 M; longer exposure resulted in further release of iodine, the band at 517 $m\mu$ increasing in intensity as the band at 275 $m\mu$ decreased.

During the procuring of the above ultraviolet and visible spectra, we found that the intensity of light in the spectrometer, incident on the sample, was not sufficient to cause any noticeable amount of reaction; the

construction of the spectrometer was such that the light from the radiation source passed through the monochromator before it passed through the reference and sample cells. In the same instrument, however, the source for near infrared spectrometry was positioned such that radiation from the light source passed through the sample and reference cells before it entered the monochromator; this source radiated visible light of sufficient intensity such that the reaction between cyclohexene and iodine in dilute solution in carbon tetrachloride could be brought to equilibrium within a few minutes. It was found that the concentration of iodine could be measured continuously by locking the instrument at 517 m μ and continuously measuring the absorbance of iodine as the chart paper flowed and the sample was illuminated. Upon interruption of illumination, the reaction was rapidly quenched.

In cyclohexane as solvent, a colorless solution of cyclohexene diiodide, estimated to be about 0.0075 M, and made up by removing iodine from a reaction solution with crystals of sodium thiosulfate, was found to remain colorless for a period of several hours when stored in the dark at about 25^o; however, when the colorless solution was irradiated in the spectrometer, iodine was rapidly eliminated from the diiodide and the reaction came to equilibrium in 2-3 min; the insertion of 1-cm cells filled with carbon disulfide in the path of the incident light from the near infrared source, in order to absorb radiation below 400 m μ ,

did not noticeably inhibit the rate of attainment of equilibrium.

A solution in carbon tetrachloride, 0.0101 M in iodine and 0.0582 M in cyclohexene, was illuminated in the spectrometer until equilibrium was reached, about 3 min; the concentration of iodine at equilibrium was found to be 0.0026 M, which at the given temperature, about 25°, corresponds to an equilibrium constant, K_{Eq} , of 57.0 liter-mole⁻¹. The solution was placed in a dark refrigerator for 3-4 hours; the concentration of iodine did not change. However, when the solution was exposed to ambient laboratory illumination for 12 hours at a temperature of 4° iodine concentration was found to decrease to about 0.0008 M, i.e., the equilibrium constant at 4° was 238 liter-mole⁻¹. When samples of this solution were allowed to return to 25°, the iodine concentration increased to near its original equilibrium value but did so much less rapidly in the dark than in the light.

Equilibria in Cycloalkene-Iodine Addition by N.m.r. Spectroscopy

Samples of cycloalkenes (10.0 mmoles) were weighed into 5.0-ml volumetric flasks: cyclohexene, 0.822 g; 4-methylcyclohexene, 0.962 g; 3-methylcyclohexene, 0.962 g; 4-t-butylcyclohexene, 1.383 g; 4,4-dimethylcyclohexene, 1.103 g; cyclopentene, 0.683 g. To each of the six samples, carbon tetrachloride, 1.0 ml, was added and the solution cooled in a dry ice-acetone bath. Iodine, 2.538 g. (10.0 mmoles) was added to each of

the cooled solutions and the mixture allowed to warm slowly to about 25°. When the iodine had dissolved, the solutions were made up to 5.0 ml with carbon tetrachloride. (In the case of 4,4-dimethylcyclohexene, the iodine did not completely dissolve; however, the mixture was made up to a total volume of 5.0 ml with carbon tetrachloride.) The 5-ml volumetric flasks were placed in a water bath at 25.0° under illumination for 15 minutes prior to obtaining n.m.r. spectra (Figures 1, 8, 10, 12, 14, 16). Integration of the intensities of the signals (in the region τ 4-6) for the ethylenic protons of the cycloalkene and for the methine protons geminal to iodine of the cycloalkene diiodides permitted a direct measurement of the relative amounts of cycloalkene and cycloalkene diiodide present in each case; this measurement allowed a calculation of the percentage reaction and the equilibrium constant for each of the reactions (Table IV).

Determination of Equilibrium Constants in Cycloalkene-Iodine Addition by Iodometric Analysis

Iodine, 25.3840 g (0.100 mole), was dissolved in carbon tetrachloride of sufficient amount to give one liter of solution at 25°. A 50.0-ml aliquot of this solution was pipetted into each of six 100.0-ml volumetric flasks, each flask containing a weighed amount (5.00 mmoles) of a different cycloalkene in carbon tetrachloride: cyclohexene, 0.413 g; 4-methylcyclohexene, 0.482 g; 3-methylcyclohexene, 0.482g; 4-t-butyl-

cyclohexene, 0.692 g; 4,4-dimethylcyclohexene, 0.557 g; cyclopentene, 0.343 g. Upon mixture of the two solutions, immediately, in each case, the solution was diluted, at 25° , to a volume of 100.0 ml with carbon tetrachloride to give solutions, initially, 0.050 M in each reactant. The reaction flasks were immersed in a thermostated water bath at 25.0° and illuminated.

At intervals, 10.0-ml aliquots were withdrawn from the reaction solutions and, in subdued light, analyzed for iodine: each aliquot was added to 10.0 ml of a 0.100 N standardized aqueous solution of sodium thiosulfate and 50 ml of water in a small separatory funnel; the two-phase system was vigorously shaken and the excess thiosulfate in the aqueous layer back titrated with a standardized 0.100 N aqueous solution of iodine.

After the reactions were found to have reached an equilibrium point, the reaction vessels were placed in a cold room at about 2° and illuminated for 10 hours in order to produce a concentration of diiodide in excess of the equilibrium concentration at 25.0° . Before analysis for iodine was again performed, the reaction vessels were wrapped in aluminum foil and returned to the thermostated bath at 25.0° for a period of 1-1.5 hours. The aluminum foil was removed and the solutions again illuminated as in the first part of the experiment; after about 3 hours, final analyses for iodine were performed. The titration data for these experiments, the calculated equilibrium concentrations for diiodide, and the calculated equilibrium constants are given in Table XIII.

TABLE XIII

Titration data for equilibrium constants in carbon tetrachloride at 25.0°
 Cycloalkene and iodine, each, initially, 0.050 M
 Reaction solution, 10.0 ml, quenched in 10.0 ml of 0.100 N thiosulfate

Cycloalkene	Time, hours	Back titre 0.100 N iodine, ml	(Diiodide), moles/liter	K_{Eq} , liter-mole ⁻¹
Cyclohexene	0.0	(0.0)	0.0000	-
	0.3	5.3	0.0265	-
	12.0	5.7	0.0285	61.7
	12.0	5.7	0.0285	61.7
	*	7.35	-	-
	#	5.7	0.0285	61.7
	**	5.74	0.0287	63.2
4-Methyl- cyclohexene	0.0	(0.0)	0.0000	-
	0.3	4.3	0.0215	-
	9.5	5.3	0.0265	48.0
	*	7.1	-	-
	#	5.35	0.0267	49.2
	**	5.27	0.0263	47.0
3-Methyl- cyclohexene	0.0	(0.0)	0.0000	-
	3.5	5.2	0.0260	45.2
	7.0	5.2	0.0260	45.2
	*	6.9	-	-
	#	5.1	0.0255	42.5
	**	5.23	0.0261	46.1
4- <u>t</u> -Butyl- cyclohexene	0.0	0.0	0.0000	-
	##	4.26	0.0215	25.9
4,4-Dimethyl- cyclohexene	0.0	0.0	0.0000	-
	0.7	0.6	0.0030	-
	5.5	0.8	0.0040	1.9
	11.0	0.8	0.0040	1.9
	*	1.6	-	-
	#	0.8	0.0040	1.9
	**	0.75	0.0037	1.8

TABLE XIII - Continued

Cycloalkene	Time, hours	Back titre 0.100 N		K_{Eq} , liter-mole ⁻¹
		iodine, ml	(Diiodide), moles/liter	
Cyclopentene	0.0	0.0	0.0000	-
	1.0	2.9	0.0145	-
	2.25	2.95	0.0147	11.8
	*	4.1	-	-
	#	3.0	0.0150	12.2
	**	3.42	0.0166	15.8

— *Analysis performed after illumination for 10 hours at 2°, followed by storage in dark for 1-1.5 hours. at 25.0°.

Analysis performed after illumination for 10 hours at 2°, storage in dark for 1-1.5 hours, and, finally, illumination for 3 hours at 25.0°.

**Duplicate run. Analysis performed after 12 hours in dark at 25.0° followed by illumination for 2 hours at 25.0°

Analysis performed after 12 hours in dark at 25° followed by illumination at 25.0° for two hours.

The above experiment was repeated with another 0.100 M solution of iodine (12.692 g in 500.0 ml of solution) in carbon tetrachloride and the following weighed amounts of cycloalkene: cyclohexene, 0.412 g; 4-methylcyclohexene, 0.481 g; 3-methylcyclohexene, 0.481 g; 4,4-dimethylcyclohexene, 0.552 g; cyclopentene, 0.343 g. The reaction solutions made up to 100.0 ml with carbon tetrachloride were allowed to stand at 25° in the dark for 12 hours and were then illuminated at 25.0°

for two hours before iodometric analysis. The results are included in Table XIII.

The equilibrium constants at 0.0° for the latter reaction solutions were also determined. Duplicate samples (10-ml aliquots) of the reaction solutions were cooled in an ice-water bath for 6 hours under illumination. The samples were then iodometrically analyzed as before. The results are given in Table XIV.

Determination of Equilibrium Constants for
Cyclohexene-Iodine Addition from $0.0-35.0^{\circ}$

Cyclohexene, 1.029 g (12.50 mmoles), dissolved in carbon tetrachloride was added to iodine, 3.173 g (12.50 mmoles), in carbon tetrachloride. The mixture was shaken until the iodine had dissolved and the solution at 25° made up to a volume of 250.0 ml in a volumetric flask. A number of 10 ml aliquots were taken and divided into two sets. One set was illuminated at 0° and the other set at 25° for 5-10 hours. One sample from each set was taken and illuminated at a given temperature (Table VI) for one hour before it was iodometrically analyzed. The titration data for these reactions are given in Table XV, along with the calculated values for the concentration of cyclohexene diiodide, K_{Eq} , and $-\Delta F$. Also, included in Table XV are the quantities $-\Delta F/T$ and $1/T$ which have been plotted in Fig. 17 in order to determine the enthalpy change in the addition reaction.

TABLE XIV

Titration data for equilibrium constants in carbon tetrachloride at 0.0°
 Cycloalkene and iodine, each, initially 0.050 M
 Reaction solution, 10.0 ml, quenched in 10.0 ml 0.100 N thiosulfate

Cycloalkene	Time	Back titre 0.100 N iodine, ml	(Diiodide) moles/liter	K_{Eq} , liter-mole ⁻¹
Cyclohexene	0.0	(0.0)	0.0000	-
	*	7.87	0.03935	346
	*	7.87		
4-Methyl- cyclohexene	0.0	(0.0)	0.0000	-
	*	7.47	0.0375	240
	*	7.52		
3-Methyl- cyclohexene	0.0	(0.0)	0.0000	-
	*	7.38	0.03715	225
	*	7.47		
4- <u>t</u> -Butyl- cyclohexene	0.0	(0.0)	0.0000	-
	*	6.27	0.0313	89.5
	*	6.37		
4,4-Dimethyl- cyclohexene	0.0	(0.0)	0.0000	-
	*	2.02	0.01045	6.7
	*	2.17		
Cyclopentene	0.0	(0.0)	0.0000	-
	*	5.85	0.0292	67.5
	*	5.95		

*Analysis performed after illumination for 6 hours at 0.0°.

TABLE XV

Titration data for determination of cyclohexene-iodine addition in carbon tetrachloride from 0.0-35.0° with reactants 0.050 M, Reaction solution, 10.0 ml, quenched in 10.0 ml 0.100 N thiosulfate

Temp (deg K)	Back titre 0.100 N iodine, ml	(Diiodide), moles/liter	K_{Eq} , liter-mole ⁻¹	$-\Delta F$ kcal/mole	$-\Delta F/T$ (x 10 ³)	$1/T$ (x 10 ³)
273.2	7.77	0.03885	313	3.14	11.5	3.66
	7.87	0.03935	346	3.19	11.7	
278.2	7.47	0.03735	233	3.03	10.9	3.59
	7.35	0.03675	209	2.97	10.7	
283.2	7.05	0.03525	162	2.88	10.2	3.53
	7.07	0.03535	164	2.88	10.2	
288.2	6.67	0.03335	120	2.76	9.6	3.47
	6.60	0.03300	114	2.73	9.5	
293.2	6.35	0.03175	95.3	2.66	9.1	3.41
	6.05	0.03025	77.7	2.55	8.7	
298.2	5.75	0.02875	63.5	2.48	8.3	3.35
	5.75	0.02875	63.5	2.48	8.3	
303.2	5.34	0.02670	49.2	2.36	7.8	3.30
	5.33	0.02665	48.9	2.36	7.8	
308.2	4.87	0.02435	37.0	2.22	7.2	3.24
	4.91	0.02455	37.9	2.24	7.3	

Rate of Cyclohexene-Iodine Addition and
Equilibrium Constants in Various Solvents

Iodine, 1.270 g (5.00 mmoles), was dissolved in 45 ml of carbon tetrachloride at 25° in a 100.0-ml volumetric flask. Cyclohexene, 1.00 ml (10.0 mmoles), was pipetted into a 100.0-ml volumetric flask containing some carbon tetrachloride and the solution was made up to the mark at 25°; a 50.0-ml aliquot of the solution of cyclohexene was, in one portion, rapidly added to the solution of iodine in the dark; immediately, the solution was made up to a volume of 100.0 ml with carbon tetrachloride and placed in a thermostated bath at 25.0° with the vessel wrapped in aluminum foil. At intervals, in subdued light, 10.0-ml aliquots were withdrawn from the reaction solution and in dim light iodometrically analyzed as previously described.

In the same way, reaction solutions, initially, 0.050 M in both iodine and cyclohexene, were made up in benzene, methylene chloride, and nitrobenzene, as solvents, and the extent of reaction determined at intervals. In each case, the solutions were allowed to undergo reaction in the dark at 25.0° for a period of 3 days; finally, to ensure that equilibrium positions had been reached, the solutions were illuminated for one day before final iodine analyses were performed.

The titration data for these rate studies, the calculated iodine concentration, $(a - x)$, its reciprocal, $1/(a - x)$, the equilibrium constant and the percentage approach to equilibrium at various times are given in Table XVI. In addition, the extent of reaction in mesitylene was determined.

TABLE XVI

Titration data for rate studies and equilibrium constants in various solvents
 at 25.0°. Cyclohexene and iodine, each initially, 0.050 M.
 Reaction solution, 10.0 ml, quenched in 10.0 ml 0.100 N thiosulfate.
 Reaction in dark in undegassed solvents.

Solvent	Time, min	Back titre 0.100 N iodine, ml	(a - x)≡ [iodine], moles/liter	Approach to equilibrium, %	$\frac{1}{(a-x)}$ liter - mole ⁻¹	K _{Eq} ,
Carbon tetrachloride	0.0	(0.0)	0.0500	0.0	20.000	-
	3.0	0.15	0.0493	2.6	20.305	-
	12.5	0.35	0.0483	6.15	20.725	-
	28.0	0.60	0.0470	10.5	21.277	-
	65.0	1.10	0.0445	19.3	22.472	-
	125	1.75	0.0413	30.7	24.243	-
	300	3.00	0.0350	52.7	-	-
	820	4.45	0.0278	78.1	-	-
	1455	5.05	0.0248	88.6	-	-
	4300	5.70	0.0215	100.0	-	61.7
	*	5.60	-	-	-	57.8
Benzene	0.0	(0.0)	0.0500	0.0	20.00	-
	15.0	0.30	0.0485	7.5	20.62	-
	19.0	0.35	0.0483	9.0	20.70	-
	30.0	0.50	0.0475	12.5	21.05	-
	60.0	0.90	0.0455	22.5	21.98	-
	121	1.70	0.0415	42.5	24.10	-
	320	2.45	0.0378	61.5	26.46	-
	1200	3.90	0.0305	98.0	-	-
	4300	4.00	0.0300	100.0	-	22.2
	*	4.00	-	-	-	22.2
Methylene chloride	0.0	(0.0)	0.0500	0.0	20.00	-
	2.5	0.80	0.0460	14.2	21.74	-
	5.0	1.45	0.0428	25.7	23.36	-
	13.5	2.55	0.0373	45.2	26.81	-
	25.0	3.50	0.0325	62.0	30.77	-
	60.0	4.60	0.0270	81.5	37.03	-
	150	5.35	0.0233	94.6	-	-
	1140	5.67	0.0217	100.0	-	60.0
	4300	5.65	-	-	-	59.4
	*	5.60	-	-	-	57.8

TABLE XVI - Continued

Solvent	Time, min	Back titre 0.100 N iodine, ml	$(a-x) =$ [iodine], moles/liter	Approach to equilibrium, %	$1/(a-x)$	K_{Eq} , liter- mole ⁻¹
Nitrobenzene	0.0	(0.0)	0.0500	0.0	-	-
	2.25	4.85	0.0258	94.0	-	-
	5.75	5.20	-	-	-	45.1
	30.0	5.10	0.0245	100.0	-	42.5
	60.0	5.10	-	-	-	42.5
	1020	5.17	-	-	-	44.0
	1025	5.25	-	-	-	46.2
	4300	4.70	-	-	-	-
	4300	4.80	-	-	-	-
	*	4.25	-	-	-	-
Mesitylene	0.0	(0.0)	0.0500	-	-	-
	30 [#]	3.25	0.0338	-	-	-
	180 ^{##}	4.00	0.0300	-	-	22.2

*Analysis performed after illumination for one day with the 200 watt tungsten filament lamp about 15 cm above the thermostated water bath.

[#]Analysis performed after 30 min in daylight.

^{##}Analysis performed after 3 hours illumination at 25.0°.

The percentage reaction and the equilibrium constant for the reaction in each of these solvents has been already presented in Table VIII. The percentage approach to equilibrium with time has been plotted in Fig. 18. In Fig. 19, $1/(a-x)$ has been plotted versus time in minutes for the initial stages of the reaction in the several solvents studied; from the

slope of the plot a value for an assumed bimolecular rate constant (k_2) was obtained in each case (Table IX).

Rate of Cyclohexene-Iodine Addition in
Degassed and Undegassed Solvents

At 25° in the dark, a 50.0-ml aliquot of a 0.100 M solution of iodine (25.384 g of iodine made up to one liter) in carbon tetrachloride was combined with a 50.0-ml aliquot of a 0.100 M solution of cyclohexene (0.823 g made up to 100.0 ml) in carbon tetrachloride to give a reaction solution, initially, nearly 0.050 M in each of the reactants, iodine, and cyclohexene. About half of the reaction solution was set aside in the dark at 25°.

The other half of the reaction solution, contained in a 100-ml flask, wrapped completely in aluminum foil, was placed on a high vacuum line; however, before the stopcock was opened and the flask evacuated, the solution it contained was frozen by immersion in liquid nitrogen for about five minutes. While still immersed in liquid nitrogen, the stopcock was opened and the reaction flask evacuated; the stopcock was closed, the liquid nitrogen bath removed, and the solution allowed to warm to room temperature in a water bath at 25°. Alternately freezing and thawing, with pumping only during the frozen periods, the solution was twice more degassed to a final pressure of about 0.2 mm, the whole process requiring about 45 min.

1. The following are the results of the first two years of the project:

1991-1992: 100% success rate, 100% of the project.

1992-1993: 100% success rate, 100% of the project.

2. The following are the results of the first two years of the project:

1991-1992: 100% success rate, 100% of the project.

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3. The following are the results of the first two years of the project:

1991-1992: 100% success rate, 100% of the project.

1992-1993: 100% success rate, 100% of the project.

4. The following are the results of the first two years of the project:

1991-1992: 100% success rate, 100% of the project.

1992-1993: 100% success rate, 100% of the project.

5. The following are the results of the first two years of the project:

1991-1992: 100% success rate, 100% of the project.

1992-1993: 100% success rate, 100% of the project.

6. The following are the results of the first two years of the project:

1991-1992: 100% success rate, 100% of the project.

1992-1993: 100% success rate, 100% of the project.

7. The following are the results of the first two years of the project:

1991-1992: 100% success rate, 100% of the project.

1992-1993: 100% success rate, 100% of the project.

8. The following are the results of the first two years of the project:

After storage of the degassed solution for a further 45 min in the dark beside the undegassed portion of the reaction solution, both solutions were analyzed in the usual manner: 10.0-ml aliquots were withdrawn from the reaction solution, reaction was quenched in excess sodium thiosulfate, 10.0 ml of a 0.100 N aqueous solution, and excess thiosulfate was back titrated with a 0.100 N aqueous solution of iodine, in subdued light.

To ensure that both portions of the reaction solution had the same concentrations of reactants at equilibrium, both portions were placed in a thermostated bath at 25.0° and illuminated for 12 hours, before final analyses for iodine were performed. The titration data for the above experiment, and the calculated extent of reaction at various times of reaction are given in Table XVII.

In another experiment, iodine, 0.2092 g (0.825 mmole), was dissolved in 90 ml of cyclohexane; in the dark, cyclohexene, 3.1614 g (38.5 mmole), was added and in subdued light the solution immediately made up to a volume of 100.0 ml. At once, a 25.0-ml aliquot was taken and diluted to a volume of 50.0 ml, to give a reaction solution, initially, 0.00413 M in iodine and 0.1925 M in cyclohexene.

In the dark, a portion of the reaction solution was degassed in the manner previously described; after 90 min in the dark at 25.0° , spectrophotometric analysis for iodine showed the reaction to have

and as a result, the entire population of the country is
 suffering from the same disease. The only way to
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TABLE XVII

Titration data for comparison of reaction rates in presence and in absence of oxygen dissolved in solvent, carbon tetrachloride.

Cyclohexene and iodine, each, initially, 0.050 M.

Reaction solution, 10.0 ml, quenched in 10.0 ml 0.100 N thiosulfate.

Solution	Time, min	Back titre 0.100 N iodine, ml	(Diiodide), moles/liter	Extent of reaction, %
Not Degassed	0.0	(0.0)	0.0000	0.0
	100.0	1.55	0.00775	15.4
	105.0	1.55	0.00775	15.4
	*	5.70	0.0285	57.0
Degassed	0.0	(0.0)	0.0500	0.0
	90.0	5.05	0.02525	50.05
	110.0	5.05	0.02525	50.05
	*	5.70	0.0285	57.0

*Performed after solution was illuminated for 12 hours at 25.0°

proceeded to an extent of 71%. In contrast, a second portion of the reaction solution which had not been degassed was found after 120 min in the dark at 25.0° to have undergone reaction to the extent of only 0.5%; after 1200 min under the same conditions, reaction had proceeded

Table 1

Summary of the results of the experiments on the effect of the concentration of the solution on the rate of the reaction. The results are given in the following table. The rate of the reaction was measured by the method described in the text.

Table 1				
Summary of the results of the experiments on the effect of the concentration of the solution on the rate of the reaction.				
Concentration of the solution (M)	Rate of the reaction (sec ⁻¹)	Concentration of the solution (M)	Rate of the reaction (sec ⁻¹)	Concentration of the solution (M)
0.1	0.001	0.2	0.002	0.3
0.2	0.002	0.3	0.003	0.4
0.3	0.003	0.4	0.004	0.5
0.4	0.004	0.5	0.005	0.6
0.5	0.005	0.6	0.006	0.7
0.6	0.006	0.7	0.007	0.8
0.7	0.007	0.8	0.008	0.9
0.8	0.008	0.9	0.009	1.0
0.9	0.009	1.0	0.010	1.1
1.0	0.010	1.1	0.011	1.2

The results of the experiments on the effect of the concentration of the solution on the rate of the reaction are given in the following table. The rate of the reaction was measured by the method described in the text. The results show that the rate of the reaction increases with the concentration of the solution. The rate of the reaction is proportional to the concentration of the solution. The results are given in the following table.

to an extent of 6.5%. Finally, a third portion of the reaction solution was illuminated at 25.0° for 3 min; spectrophotometric analyses for iodine showed that the reaction had proceeded to an extent of 88.5%.

Effect of Tetra-*n*-butylammonium Iodide on Rate of Cyclohexene-Iodine Addition

Iodine, 2.7934 g (11.0 mmoles), in a 100.0 ml volumetric flask was dissolved by the addition of 20.0 ml of methylene chloride and sufficient carbon tetrachloride to give 100.0 ml of solution. Cyclohexene, 0.9048 g (11.0 mmoles), was dissolved in 20.0 ml of methylene chloride and sufficient carbon tetrachloride to give 100.0 ml of solution. Three other solutions were prepared: (i) 10.0 ml of methylene chloride was diluted to 50.0 ml with carbon tetrachloride; (ii) tetra-*n*-butylammonium iodide, 0.0924 g (0.25 mmoles), was dissolved in 10.0 ml of methylene chloride and the solution made up to 50.0 ml with carbon tetrachloride; (iii) a 25.0-ml aliquot of solution 'ii' was diluted to 50.0 ml by addition of solution 'i'. All of the above solutions were prepared at about 25° and the reactions below carried out at the same temperature.

Three reaction solutions were prepared: a 25.0-ml aliquot of the iodine solution was combined with a 5.0-ml aliquot of the methylene chloride-carbon tetrachloride solution (i) and, then, a 25.0-ml aliquot of the cyclohexene solution added rapidly and the combined solutions thoroughly shaken: likewise, reaction solutions were prepared using

5.0-ml aliquots of the solutions 'ii' and 'iii' above. At intervals, 10.0-ml aliquots were withdrawn from the reaction solutions and reaction quenched by adding the aliquots to 10.0-ml aliquots of a 0.100 N solution of sodium thiosulfate in 25 ml of water, the two-phase system being vigorously stirred; excess thiosulfate was back-titrated with a 0.100 N solution of iodine. The reaction flask, in all cases, was wrapped in aluminum foil; operations, in all cases, were performed in subdued light. The titration data for these experiments are presented in Table XVIII along with calculated concentrations of cyclohexene diiodide. The rates of formation of cyclohexene diiodide are plotted in Fig. 20.

Effect of Tetra-n-butylammonium Iodide
and Tetra-n-butylammonium Perchlorate on
Rate of Cyclohexene-Iodine Addition

Iodine, 2.7926 g (11.0 mmoles) in a 100.0-ml volumetric flask was dissolved by the addition of 20.0 ml of methylene chloride and sufficient carbon tetrachloride to give 100.0 ml of solution. Cyclohexene, 0.9048 g (11.0 mmoles), was dissolved in 20.0 ml of methylene chloride and sufficient carbon tetrachloride to give 100.0 ml of solution. Three other solutions were prepared: (i) 10.0 ml of methylene chloride was diluted to 50.0 ml with carbon tetrachloride; (ii) tetra-n-butylammonium iodide, 0.0924 g (0.25 mmoles), was dissolved in 10.0 ml of methylene

TABLE XVIII

Titration data for studies of effect of tetra-n-butylammonium iodide and perchlorate on rate of cyclohexene-iodine addition in dark at 25°, each reactant, 0.050 M.

Undegassed solvent (carbon tetrachloride:methylene chloride :: 4:1)

Reaction solution, 10.0 ml, quenched in 10.0 ml 0.100 N thiosulfate

Salt	(Salt), moles/liter	Time, sec	Back titre 0.100 N iodine, ml	(Diiodide), moles/liter
None		0	(0.0)	0.0000
		60	0.15	0.00075
		135	0.20	0.00100
		220	0.25	0.00125
		300	0.28	0.00140
		48 hours	5.80	0.0290
Iodide	0.000225	0	(0.0)	0.0000
		70	0.20	0.00100
		145	0.35	0.00175
		220	0.50	0.00250
		320	0.70	0.00350
		48 hours	5.80	0.0290
Iodide	0.000450	0	(0.0)	0.0000
		75	0.27	0.00135
		160	0.60	0.00300
		285	0.95	0.00475
		365	1.20	0.00600
		48 hours	5.80	0.0290

TABLE XVIII - Continued

Salt	(Salt), moles/liter	Time, sec	Back titre 0.100 N iodine, ml	(Diiodide), moles/liter
None		0	(0.0)	0.0000
		65	0.10	0.00050
		160	0.15	0.00075
		255	0.25	0.00125
		365	0.30	0.00150
		14 hours	5.10	0.02550
		*	5.80	0.0290
Iodide	0.00045	0	(0.0)	0.0000
		90	0.35	0.00175
		170	0.62	0.00310
		265	0.90	0.00450
		345	1.10	0.00550
		14 hours	5.60	0.0280
Perchlorate	0.00045	0	(0.0)	0.0000
		70	0.25	0.00125
		145	0.50	0.00250
		215	0.65	0.00325
		285	0.85	0.00425
		50 hours	5.70	0.285

*Performed after solution illuminated for 10 min at 25°

chloride and the solution diluted to 50.0 ml with carbon tetrachloride;

(iii) tetra-n-butylammonium perchlorate, 0.0862 g (0.25 mmoles), was

dissolved in 10.0 ml of methylene chloride and the solution diluted to

50.0 ml with carbon tetrachloride. All of the above solutions were prepared at about 25° and the reactions below carried out at the same temperature.

Three reaction solutions were prepared and analyzed as described on pages 132 - 133, using now an aliquot of one of the three solutions, (i), (ii), and (iii), above.

The titration data for these experiments are given in Table XVIII along with calculated concentrations of cyclohexene diiodide; the rates of formation of cyclohexene diiodide are plotted in Fig. 21.

Reaction of Cyclohexene Diiodide with Excess Halide Ion

A solution of cyclohexene diiodide was prepared: cyclohexene, 0.3298 g (4.00 mmoles), was dissolved in chloroform, iodine, 1.0163 g (4.00 mmoles), added, and the solution made up to 100.0 ml with chloroform; this solution was illuminated at 0° for one hour and then allowed to come to 25° in the dark, whereupon titrimetric analysis showed the solution to be 0.028 M in cyclohexene diiodide, and 0.012 M in iodine.

A 10.0 ml aliquot of this solution of cyclohexene diiodide was added (i) to tetra-n-butylammonium iodide, 1.48 g (4.0 mmoles), dissolved in 25 ml of chloroform in a separatory funnel, (ii) to tetra-n-butylammonium bromide, 1.29 g (4.0 mmoles), dissolved in 25 ml of chloroform in a separatory funnel (iii) to tetraethylammonium chloride, 0.66 g (4.0 mmoles),

in 25 ml of chloroform in a separatory funnel. After about one minute, 10.0 ml of a 0.100 N aqueous solution of sodium thiosulfate was added to each of the reaction solutions, the two-phase system vigorously shaken to remove free iodine, the chloroform layer drained off, and the aqueous layer back-titrated with a 0.100 N aqueous solution of iodine. These reactions were repeated varying the time of reaction. The results are tabulated in Table XIX.

TABLE XIX

Titration data for reaction of cyclohexene diiodide with excess halide ion in chloroform at 25°. Initially, cyclohexene diiodide, 0.028 M and iodine, 0.012 M.

Reaction solution, 10.0 ml, quenched in 10.0 ml of 0.100 N thiosulfate.

Reaction	Time	Back titre 0.100 N iodine, ml	Net titre 0.100 N thiosulfate, ml	Percentage haloiodide
$C_6H_{10}I_2 + 10 I^{\ominus}$	0	(7.6)	(2.4)	(70)
	1 min	2.05	7.95	0.6
$C_6H_{10}I_2 + 10 Br^{\ominus}$	0	(7.6)	(2.4)	(70)
	1 min	2.10	7.90	1.3
	1 day	2.30	7.70	3.8
$C_6H_{10}I_2 + 10 Cl^{\ominus}$	0	(7.6)	(2.4)	(70)
	1 min	5.85	4.15	48
	1 min	5.85	4.15	48
	5 min	2.45	7.55	5.5
	2 hours	5.20	4.80	40
	1 day	7.90	2.10	74

Formation of Cyclohexene *trans*-Chloroiodide from
Cyclohexene, Iodine, and Excess Chloride Ion

Cyclohexene, 0.822 g (10.0 mmoles), iodine, 2.538 g (10.0 mmoles), and tetraethylammonium chloride, 16.6 g (100 mmoles) were combined in 90 ml of chloroform. The reaction mixture was brought into solution by the addition of methylene chloride, sufficient to give 100.0 ml of solution. After 60 hours, iodometric titration showed only 40% of the original iodine to be present in titratable form. The solution was evaporated to give a brown semi-solid mass which was extracted with carbon tetrachloride; the extract, in turn, upon evaporation gave a pale yellow liquid (1.6 g) which was shown by g.l.c. analysis to correspond to a 50-50% mixture of carbon tetrachloride and cyclohexene *trans*-chloroiodide. An n.m.r. spectrum (Fig. 22) of the liquid mixture was identical with that of an authentic sample of cyclohexene *trans*-chloroiodide. The symmetrical band centered about τ 5.60 for the protons geminal to halogen (137) had an integrated intensity 0.25 that of the bands at higher field for the methylenic protons.

Measurement of Equilibria in the Reaction of
Cyclohexene with Tetraalkylammonium Diiodohalides

N.m.r. Method. A 2.00 M solution of cyclohexene was prepared by solution of cyclohexene 4.108 g (50.0 mmoles), in sufficient chloroform (29.518 g, 248 mmoles) to give 25.0 ml of solution.

Three solutions were made up, as follows: (i) Tetra-n-butylammonium iodide, 3.695 g (10.0 mmoles), was dissolved in 5.0 ml of the solution of cyclohexene; iodine, 2.539 g (10.0 mmoles), was added and the mixture shaken to obtain solution. (ii) Tetra-n-butylammonium bromide, 3.226 g (10.0 mmoles), was dissolved in 5.0 ml of the solution of cyclohexene; iodine, 2.540 g (10.0 mmoles), was added and the mixture shaken to obtain solution. (iii) Tetra-n-butylammonium iodide, 3.695 g (10.0 mmoles), was dissolved in 5.0 ml of the solution of cyclohexene; iodine monochloride, 1.629 g (10.0 mmoles), was added and the mixture shaken to obtain solution. These solutions (i - iii) had a total volume, each, of about 8.0 ml; hence they were about 1.25 M in each reactant.

After standing in the dark at about 25° for 65 hours, the solutions were analyzed by n.m.r. spectroscopy. In the n.m.r. spectrum of the first solution, there was no evidence that any reaction had occurred between cyclohexene and triiodide ion: only the signals characteristic of chloroform, cyclohexene, and tetra-n-butylammonium ion were present, and integration of the peaks at τ 2.4 for chloroform, at τ 4.2 for cyclohexene, and at τ 6.3-6.7 for the α -methylenic protons of the tetra-n-butylammonium ion indicated the original proportion of cyclohexene to be still present. The n.m.r. spectrum of the second solution showed, in addition to the absorption peaks found in the spectrum of the first solution, a small peak at τ 5.2 (half-width, about 10 c.p.s.) in the

region where the methine protons of cyclohexene trans-bromiodide absorb. The ratio of the intensity of the signal at τ 5.2 to that for the ethylenic protons of cyclohexene at τ 4.2 was 1.0:6.3, indicating that 13.7% of the cyclohexene had reacted with diiodobromide ion with the formation of cyclohexene bromiodide. In the case of the third reaction, the n.m.r. spectrum of the solution showed, in addition to the signals present in the spectrum of the first solution, a multiplet at τ 6.85 (half-width about 15 c.p.s.) in the region where the methine protons of cyclohexene trans-chloriodide absorb (137). The ratio of the intensity of the signal at τ 6.85 to that for the ethylenic protons of cyclohexene at τ 4.2 was 1.0:1.3, indicating that 43.5% of the cyclohexene had reacted with diiodochloride ion with the formation of cyclohexene chloriodide.

Titrimetric Method. The following solutions (i-viii) were analyzed iodometrically by taking 10.0-ml aliquots, at intervals, and adding them to a 125-ml separatory funnel containing a 10.0-ml aliquot of a 0.100 N aqueous solution of sodium thiosulfate and 20 ml of water. The two-phase mixture was shaken vigorously, but briefly, to remove unreacted halogen from the chloroform layer. The settled chloroform layer was drained off and the excess sodium thiosulfate in the aqueous layer back-titrated with 0.100 N iodine. The titration results are given in Table XX.

(i) Reaction between cyclohexene diiodide and tetra-n-buylammonium iodide.

Cyclohexene, 0.8242 g (10.00 mmoles), was dissolved in chloroform in a 100.0-ml volumetric flask; iodine, 2.5390 g (10.00 mmoles), was added and the solution obtained made up to 100.0 ml with chloroform. The solution was illuminated at 0° for about one-half hour and then allowed to warm to 25° in the dark. A 25.0-ml aliquot of this solution was added to tetra-n-butylammonium iodide, 0.9240 g (2.50 mmoles), dissolved in chloroform, and the reaction solution made up to 50.0 ml with chloroform.

(ii) Reaction between cyclohexene and tetra-n-butylammonium triiodide.

A 25.0-ml aliquot of a 0.100 M solution of cyclohexene (2.50 mmoles) in chloroform was added to a solution in chloroform of tetra-n-butylammonium iodide, 0.9237 g (2.50 mmoles), and iodine, 0.6346 g (2.50 mmoles), and the combined solutions made up to 50.0 ml.

(iii) Reaction between cyclohexene diiodide and tetra-n-butylammonium bromide.

A 25.0-ml aliquot of the solution of cyclohexene diiodide prepared in (i) above was added to tetra-n-butylammonium bromide, 0.8061 g (2.50 mmoles), dissolved in chloroform, and the reaction solution made up to 50.0 ml with chloroform.

(iv) Reaction between cyclohexene and tetra-n-butylammonium diiodobromide.

A 25.0-ml aliquot of a 0.100 M solution of cyclohexene (prepared

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by dilution to 100.0 ml with chloroform of 0.8217 g, 10.00 mmoles, of cyclohexene) was added to a solution in chloroform of tetra-n-butylammonium bromide, 0.8069 g (2.50 mmoles), and iodine, 0.6350 g (2.50 mmoles), and the combined solution made up to 50.0 ml by the addition of chloroform.

(v) Reaction between cyclohexene diiodide and tetraethylammonium chloride.

A 25.0-ml aliquot of the solution of cyclohexene diiodide prepared in (i) above, was added to tetraethylammonium chloride, 0.4148 g (2.50 mmoles), dissolved in chloroform, and the reaction solution made up to 50.0 ml with chloroform. Reddish-black needles, presumably a trihalide salt, precipitated out so the solution was diluted one-fold with methylene chloride to give a solution.

(vi) Reaction between cyclohexene and tetraethylammonium diiodochloride.

A 25.0-ml aliquot of the 0.100 M solution of cyclohexene from (iv), above, was added to a solution in chloroform of tetraethylammonium chloride, 0.4144 g (2.50 mmoles), and iodine, 0.6350 g (2.50 mmoles), and the combined solutions made up to 50.0 ml with chloroform. As in (v), however, it was found necessary to add solvent to maintain solution; again, the solution was diluted one-fold with methylene chloride.

(vii) Reaction between cyclohexene and tetra-n-butylammonium diiodochloride .

A 25.0-ml aliquot of the 0.100 M solution of cyclohexene , from (iv) , above , was added to a 25.0-ml aliquot of a solution of tetra-n-butylammonium diiodochloride (prepared by solution of iodine monochloride , 1.6254 g , 10.00 mmoles, and tetra-n-butylammonium iodide , 3.6953 g , 10.00 mmoles , in sufficient chloroform to give 100.0 ml of solution).

(viii) Reaction between cyclohexene chloriodide and tetra-n-butylammonium iodide .

A 0.100 M solution of cyclohexene chloriodide was prepared by the addition of a solution in chloroform of iodine monochloride , 1.6255 g , (10.00 mmoles) , to a solution , in chloroform , of cyclohexene , 0.8228 g (10.00 mmoles) , the combined solutions being made up to a volume of 100.0 ml with chloroform. A 25.0-ml aliquot of this solution was added to a 25.0-ml aliquot of a 0.100 M solution of tetra-n-butylammonium iodide (prepared by solution of 3.6943 g , 10.00 mmoles , of tetra-n-butylammonium iodide in sufficient chloroform to give 100.0 ml of solution).

TABLE XX

Titration data for measurement of equilibria in the reactions of cyclohexene with tetraalkylammonium diiodohalides in chloroform* at 25°.

Reaction solution, 10.0 ml*, quenched in 10.0 ml 0.100 N thiosulfate.

Reactants [#]	Time	Back titre 0.100 N iodine, ml	Per cent cyclohexene haloiodide at equilibrium
(i) $C_6H_{10}I_2 + Bu_4N^+I^-$	0	-	-
	15 min	0.0	0
(ii) $C_6H_{10} + Bu_4N^+I_3^-$	0	0.0	-
	30 min	0.0	0
	22 hours	0.0	0
(iii) $C_6H_{10}I_2 + Bu_4N^+Br^-$	0	-	
	10 min	0.75	
	3 hours	1.45	14.5
	1 day	1.60	16.0
	1 week	1.50	15.0 (13.7) [@]
(iv) $C_6H_{10} + Bu_4N^+I_2Br^-$	0	0.0	
	1 hours	0.45	
	18 hours	1.05	
	42 hours	1.55	15.5
	4 days	1.63	16.3 (13.7) [@]
(v)* $C_6H_{10}I_2 + Et_4N^+Cl^-$	0	-	
	20 min	3.45	
		4.90	
	1 day	5.25	52.5
	1 week	5.25	52.5
(vi)* $C_6H_{10} + Et_4N^+I_2Cl^-$	0	0.0	
		5.05	
	1 day	5.20	52.0
	1 week	5.25	52.5

TABLE XX - Continued

Reactants [#]	Time	Back titre 0.100 N iodine, ml	Per cent cyclohexene haloiodide at equilibrium
(vii) C ₆ H ₁₀ + Bu ₄ N [⊕] I ₂ Cl [⊖]	0 15 min 4 hours 15 hours 3 days	0.0 2.7 4.7 4.9 4.9	— — — 49.0 49.0 (43.5) [@]
(viii) C ₆ H ₁₀ ICl + Bu ₄ N [⊕] I [⊖]	0 6 min 4 hours 15 hours 3 days	— 8.9 6.3 5.0 4.9	— — — 50.0 49.0 (43.5) [@]

*In reaction v and vi, in order to maintain reactants in solution, the reaction solution was diluted one-fold with methylene chloride; hence in these cases 20.0 ml aliquots were taken.

[#]Reactants, each, initially, 0.050 M except in v and vi*.

[@]Values from n.m.r. method.

Measurement of Equilibria in the Reaction of Cyclohexene with Tetra-n-butylammonium Tetraiodohalides

(i) Reaction between cyclohexene and tetra-n-butylammonium pentaiodide.

Cyclohexene, 0.8220 g (10.0 mmoles), was dissolved in chloroform and the solution made up to 100.0 ml to give a 0.100 M solution. Tetra-n-

butylammonium iodide, 0.9235 g (2.50 mmoles), and iodine, 1.2698 g (5.00 mmoles), were dissolved in chloroform, 25.0 ml of the 0.100 M cyclohexene solution added, and the combined solutions made up to a volume of 50.0 ml with chloroform.

(ii) Reaction between cyclohexene and tetra-n-butylammonium tetraiodobromide.

Tetra-n-butylammonium bromide, 0.8060 g (2.50 mmoles), and iodine, 1.2702 g (5.00 mmoles), were dissolved in chloroform, 25.0 ml of the 0.100 M solution of cyclohexene prepared in (i), above, was added and the combined solution made up to 50.0 ml with chloroform.

(iii) Reaction between cyclohexene and tetraethylammonium tetraiodochloride.

Iodine, 0.6347 g (2.5 mmoles), was dissolved in a 25.0-ml aliquot of a 0.100 M solution of tetra-n-butylammonium diiodochloride in chloroform (prepared for reaction vii, p. 143) and to this solution a 25.0-ml aliquot of the 0.100 M solution of cyclohexene prepared in (i), above, was added to give a total volume of 50 ml of solution.

Reaction solutions, (i) - (iii), were analyzed for free halogen as described above, with the exception that 20.0 ml aliquots of the aqueous solution of sodium thiosulfate were used. The results are given in the accompanying table (XXI).

TABLE XXI

Titration data for measurement of equilibria in the reactions of cyclohexene with tetra-n-butylammonium tetraiodohalides in chloroform in dark at 25°
Reaction solution, 10.0 ml, quenched in 20.0 ml 0.100 N thiosulfate.

Reactants	Time	Back titre 0.100 N iodine , ml	Per cent cyclohexene haloiodide at equilibrium
(i) C ₆ H ₁₀ I ₅ [⊖]	0	0.00	—
	15 min	0.00	—
	10 days	0.20	0
	(in daylight)		
(ii) C ₆ H ₁₀ I ₄ Br [⊖]	0	0.00	—
	30 min	5.25	—
	1 day	5.70	57.0
	2 days	5.70	57.0
	10 days	5.60	56.0
(iii) C ₆ H ₁₀ I ₄ Cl [⊖]	0	0.00	—
	1.5 hours	7.95	—
	17 hours	8.95	89.5
	2 days	9.10	91.0
	10 days	9.00	90.0

Reaction of Cyclohexene with Tetra-n-butylammonium
Tetraiodobromide Followed by Ultraviolet Spectrophotometry

A solution of tetra-n-butylammonium tetraiodobromide, 0.010 M, was prepared: tetra-n-butylammonium bromide, 0.0321 g (0.100 mmole), and iodine, 0.0508 g (0.200 mmole), were dissolved in methylene chloride,

sufficient to give 10.0 ml of solution. A portion of this solution was diluted 500-fold with methylene chloride to give a solution 2.0×10^{-5} M in tetraiodobromide ion; with 1-cm cells an ultraviolet spectrum of this solution showed an absorption, λ_{max} 282 m μ (absorbance 0.78) with a shoulder at 360 m μ (estimated absorbance 0.10).

A solution of tetra-n-butylammonium triiodide, 0.010 M, was prepared: tetra-n-butylammonium iodide, 0.0377 g (0.100 mmole), and iodine, 0.0254 g (0.100 mmole), were dissolved in methylene chloride, sufficient to give 10.0 ml of solution. A portion of this solution was diluted 500-fold with methylene chloride to give a solution 2.0×10^{-5} M in triiodide ion; with 1-cm cells an ultraviolet spectrum of this solution showed absorptions, λ_{max} 295 m μ (absorbance 0.97) and 365 m μ (estimated absorbance 0.41), the two broad peaks being partially superimposed (158).

A solution very nearly 1.0×10^{-5} M in tetra-n-butylammonium tetraiodobromide and 1.0×10^{-5} M in tetra-n-butylammonium triiodide was prepared: 2.00-ml aliquots of each of the 0.0100 M solutions prepared above were combined; a 0.10-ml aliquot of the combined solution was diluted with methylene chloride to a volume of 50.0 ml. With 1-cm cells, an ultraviolet spectrum of this solution showed absorptions, λ_{max} 290 m μ (absorbance 0.82) and 360 m μ (estimated absorbance 0.22), the two broad peaks being partially superimposed.

A 25.0-ml aliquot of a 0.100 M solution of cyclohexene in methylene chloride was added to a solution of iodine, 1.267 g (5.0 mmoles), and tetra-n-butylammonium bromide, 0.807 g (2.5 mmoles), in 20 ml of methylene chloride; the solution was made up to a volume of 50.0 ml with methylene chloride and allowed to stand for 3 days in the dark at 25°. A 0.020-ml aliquot of the reaction solution was diluted to 50.0 ml with methylene chloride; with 1-cm cells an ultraviolet spectrum showed absorptions, λ_{max} 292 m μ (absorbance 0.90) and 362 m μ (estimated absorbance 0.32), the two broad peaks being partially superimposed.

Reaction of Ethylene Diiodide with
Tetraethylammonium Diiodochloride

Ethylene diiodide, 2.818 g (10.0 mmoles), was added to a solution of tetraethylammonium chloride, 1.667 g (10.0 mmoles), and iodine, 2.540 g (10.0 mmoles), in methylene chloride, 2.56 ml (40.0 mmoles). After one-half hour, an n.m.r. spectrum of the reaction solution showed about 2.5-times as many moles of tetraethylammonium salt as ethylene diiodide: a triplet centered at τ 8.7, due to the 12 methyl hydrogens of the tetraethylammonium ion, and a singlet at τ 6.3, due to the 4 hydrogens of ethylene diiodide, had relative intensities 7.4 : 1.0, respectively. The singlet at τ 6.3 and a quartet centered at τ 6.65, due to the 8 methylene hydrogens of the tetraethylammonium ion, were superimposed on a band of weak signals in the same region; if these

signals were due entirely to the presence of ethylene chloriodide, it was estimated that this compound had formed in a yield no greater than 25%.

After 3 days in the dark, the reaction solution, which had become very viscous, was extracted with carbon tetrachloride, the extract concentrated, and an n.m.r. spectrum taken. The spectrum (Fig. 26), as was to be expected for ethylene chloriodide, had a well defined A_2B_2 pattern (159) which consisted of two series of signals, the mirror images of each other; the band of signals was situated in the region τ 6.00-6.75 and had a minimum at τ 6.37. A similar spectrum for ethylene chlorobromide has been recorded (159).

Reaction of Ethylene Diiodide and Tetraethylammonium Diiodochloride in Presence of Cyclohexene

Cyclohexene, 1.0 ml (10 mmoles), and ethylene diiodide, 2.8 g (10 mmoles), were added to a solution of tetraethylammonium chloride, 1.7 g (10 mmoles), and iodine, 2.5 g (10 mmoles), in methylene chloride. After 3 hours, the solution was evaporated, the residue extracted with carbon tetrachloride; the extract was concentrated and its n.m.r. spectrum taken; the spectrum (Fig. 27) was identical with that for cyclohexene chloriodide contaminated with about 20% ethylene diiodide. There was no evidence for the presence of ethylene chloriodide.

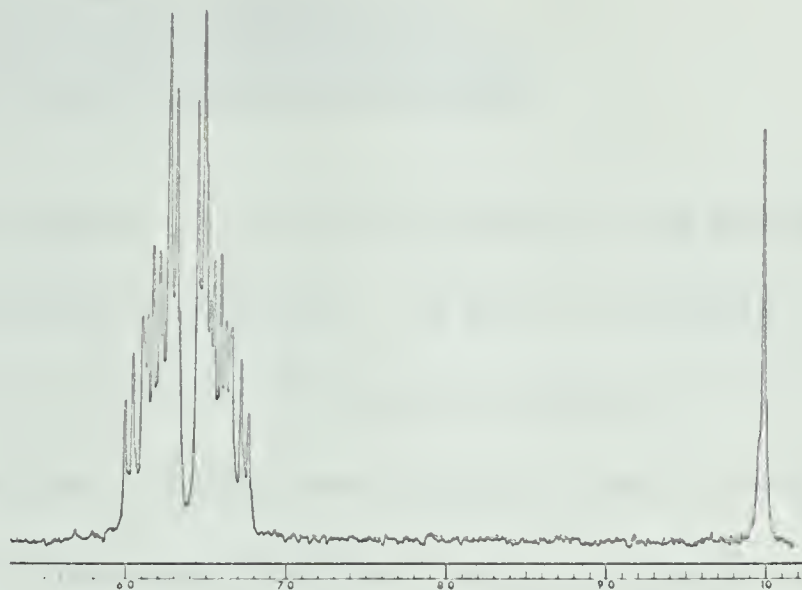


FIG. 26. N.m.r. spectrum (60 Mc.p.s.) of ethylene chloroiodide in carbon tetrachloride.

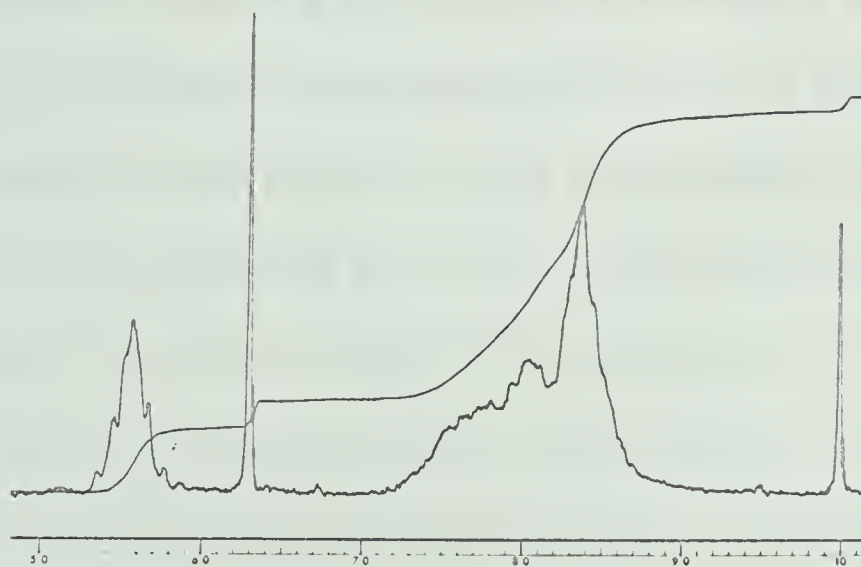


FIG. 27. N.m.r. spectrum (60 Mc.p.s.) of product of reaction of ethylene diiodide, tetraethylammonium diiodochloride, and cyclohexene: corresponding to cyclohexene trans-chloroiodide with about 20% ethylene diiodide present.

Reaction of Ethylene Diiodide with
Tetraethylammonium Diiodochloride in
Presence of Cyclohexene and Ethylene

Cyclohexene, 1.0 ml (10 mmoles), was added to a solution of tetraethylammonium chloride, 1.66 g (10.0 mmoles), and iodine, 2.54 g (10.0 mmoles), in 40 ml of methylene chloride; the solution was placed in an ice bath and ethylene was bubbled slowly through the solution; after 20 min, ethylene diiodide, 2.82 g (10.0 mmoles), was added and the solution was allowed to stand at a temperature of about 25° for 16 hours while ethylene bubbled slowly through it; large black crystals were deposited. The mixture was evaporated and the residue extracted with carbon tetrachloride; the n.m.r. spectrum of the concentrated extract (similar to that in Fig. 28) showed 15-20% as much ethylene diiodide as cyclohexene chloroiodide but no trace of ethylene chloroiodide.

A separate experiment in which a saturated solution of ethylene in chloroform was examined by n.m.r. spectroscopy revealed a concentration of ethylene of about 1.7 molar percent. Methylene chloride could not be used as solvent since ethylene was found to absorb at τ 4.50, near the position of absorption for methylene chloride, itself. If the solubility of ethylene in methylene chloride is as high in methylene chloride as in chloroform, then, the quantity of ethylene in solution in 40 ml of methylene chloride should be at least 8.5 mmoles.

Reaction of Cyclohexene with Potassium
Acetate and Iodine

Potassium acetate, 0.98 g (10.0 mmoles), iodine, 5.08 g (20.0 mmoles), and cyclohexene, 1.0 ml (10.0 mmoles), were added to 25 ml of methylene chloride and the mixture shaken for 4 days in the dark at 25°. Carbon tetrachloride was added and the mixture extracted with an aqueous solution of sodium thiosulfate; the organic layer was separated, dried, filtered, and evaporated to a syrup. Methylene chloride, 0.32 ml (5.0 mmoles) was added to the syrup. An n.m.r. spectrum (Fig. 28) in addition to absorptions at high field for methylenic protons, showed sextets centered at τ 5.88 and at τ 5.12 (spacings of signals in sextets, about 5 c.p.s.) and a sharp singlet at τ 7.95 in the region for acetoxy protons; the relative intensities of the sextets and the singlet were 1:1:~3, respectively, as expected for cyclohexene acetoxyiodide. The spectrum was identical, in fact, with the spectrum of a sample of cyclohexene trans-acetoxyiodide prepared in the usual way (194, 221) by the reaction of equimolar amounts of iodine, cyclohexene, and silver acetate. The intensity of the signal for methylene chloride in the above spectrum (Fig. 28) indicated that the reaction had proceeded to an extent greater than 50%.

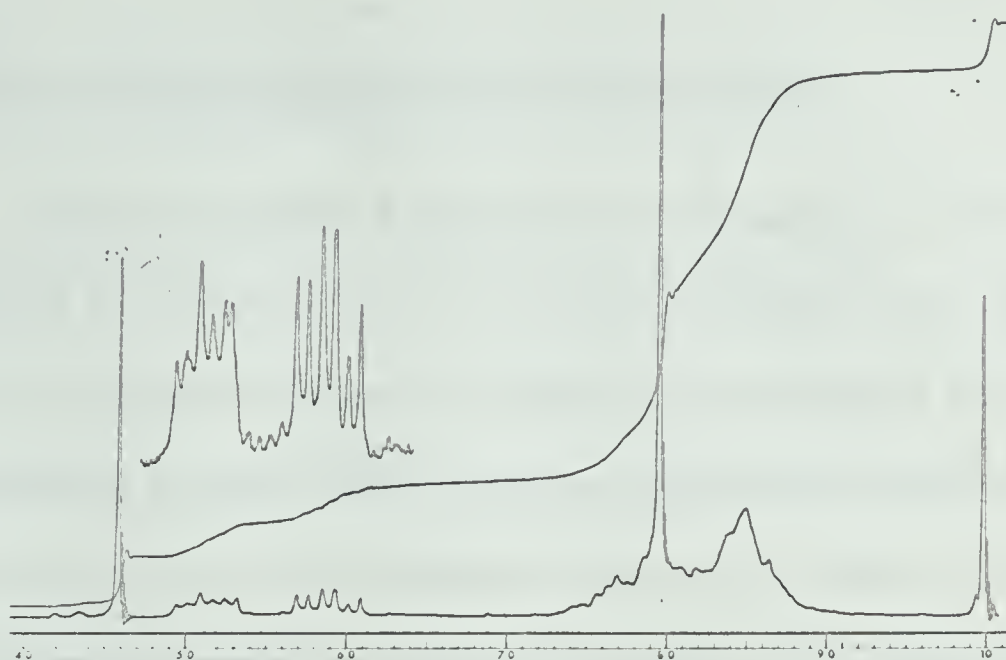


FIG. 28. N.m.r. spectrum (60 Mc.p.s.) of cyclohexene trans-acetoxiodide in methylene chloride.

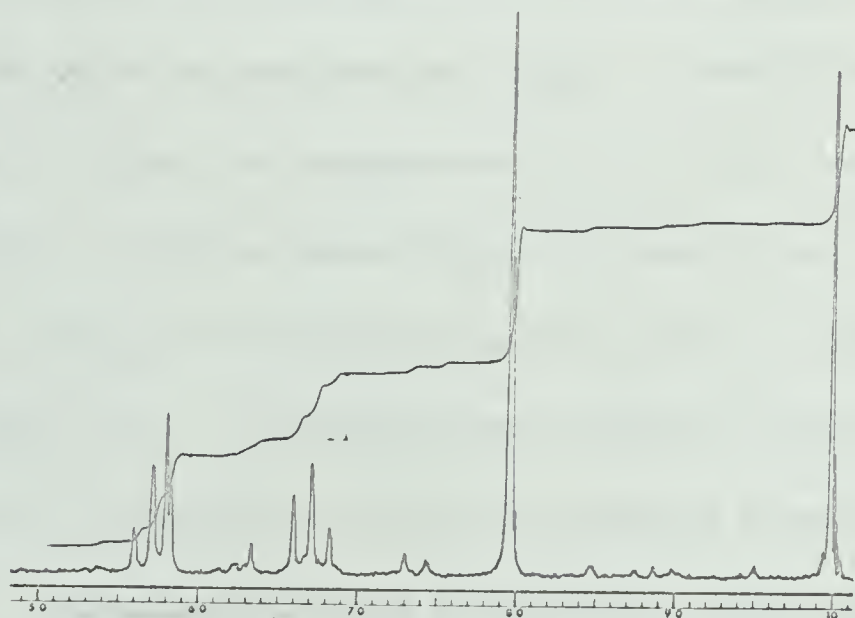


FIG. 29. N.m.r. spectrum (60 Mc.p.s.) of ethylene acetoxiodide contaminated with about 17% ethylene diacetate and about 10% ethylene diiodide.



Reaction of Ethylene Diiodide with Silver Acetate

Ethylene diiodide was added to a 5% excess of silver acetate suspended in hot acetic acid. The stirred mixture was allowed to cool to 25° and, after 20 hours in the dark, it was filtered and the filtrate evaporated to a syrup; the syrup was dissolved in diethyl ether and the solution extracted with an aqueous solution of sodium bicarbonate, followed by an aqueous solution of sodium thiosulfate; the organic layer was separated, dried, filtered, and evaporated to a syrup.

The n.m.r. spectrum of the syrup (Fig. 29) displayed a singlet at τ 7.95 (in the region for acetoxy protons), triplets centered at τ 5.70 and at τ 6.70, (with spacings in each case of about 7 c.p.s.) and a singlet at τ 5.78, superimposed on the triplet at lower field; the relative intensities of these four signals were 2:1:1:0.36, respectively. Ethylene acetoxyiodide would be expected to give rise to the triplets cited: the presence of about 17% ethylene diacetate would account for the signal at τ 5.78 (the n.m.r. spectrum of an authentic sample of ethylene diacetate did, in fact, absorb here) and for the relative intensity of the signal at τ 7.95. (Kavadias (221) has shown that in alkene acetoxyiodides, the protons geminal to an acetoxy group absorb at lower field than protons geminal to iodine). A small signal at τ 6.32 indicated the presence of less than 10% ethylene diiodide. Analysis by g.l.c. gave a chromatograph which

showed one major peak with a broad fore-peak representing about 25% of the area of the major peak.

Initial Reaction of Acetate Ion with Alkene Diiodides

A colorless solution of cyclohexene diiodide (5.0 ml of a 0.042 M solution in methylene chloride, i.e., 0.21 mmoles) was added to a solution of tetra-n-butylammonium biacetate, 0.854 g (2.5 mmoles) in 5 ml of methylene chloride. Iodine was immediately liberated; after about five minutes, iodometric titration showed that 90% of the possible amount of iodine had been eliminated.

Reaction of Cyclohexene Diiodide with Tetra-n-butylammonium Biacetate

Cyclohexene, 5.0 ml (50 mmoles), and iodine, 5.0 g (20 mmoles), were added to 50 ml of carbon tetrachloride. The mixture was shaken under illumination at 4° for 1.5 hours and the faintly purple solution obtained was added to a solution of tetra-n-butylammonium biacetate (3.0 g, 8.3 mmoles) in 200 ml of carbon tetrachloride and 20 ml of methylene chloride. The solution was shaken in the dark at 25° and after 20 hours a black precipitate had formed. The mixture was filtered and the filtrate evaporated to a brown syrup. A little diethyl ether was added, the solution chilled in a dry ice-acetone bath, and filtered to remove a black precipitate. The filtrate was evaporated to a faintly brown syrup, the

n.m.r. spectrum of which was identical to that described above for cyclohexene trans-acetoxyiodide (the presence of a small signal at τ 4.3, however, indicated the presence of about 3% cyclohexene). The yield of cyclohexene acetoxyiodide was 2.2 g (8.1 mmoles); the recovered black precipitate weighed 5.2 g (8.3 mmoles, if pure tetra-n-butylammonium triiodide).

Reaction of Equimolar Amounts of Cyclohexene and
Tetra-n-butylammonium Biacetate with Twice the
Molar Proportion of Iodine

Cyclohexene, 0.50 ml (5.0 mmoles), dissolved in 10 ml of methylene chloride, was added to a solution of iodine, 2.538 g (10.0 mmoles), and tetra-n-butylammonium biacetate, 1.809 g (5.0 mmoles), in 80 ml of methylene chloride. The solution was made up to a volume of 100.0 ml and after 12 hours in the dark at 25^o, a 10.0-ml aliquot of the reaction solution was run into 25.0 ml of a 0.100 N solution of sodium thiosulfate and back titrated with 12.8 ml of a 0.100 N solution of iodine, indicating cyclohexene acetoxyiodide had formed in a yield of 78%.

The main reaction solution was decolorized with an aqueous solution of sodium thiosulfate, the organic layer separated, washed with water, dried, and evaporated to an orange syrup. G.l.c. showed the syrup to consist of one major component, the retention time of which was identical to that for cyclohexene acetoxyiodide.

Reaction of Ethylene Diiodide with
Tetra-n-butylammonium Biacetate

Tetra-n-butylammonium biacetate, 1.82 g (5.0 mmoles), and ethylene diiodide, 1.41 g (5.0 mmoles), were dissolved in 50 ml of methylene chloride. After one hour in the dark at 25°, the solution was evaporated to a dark brown syrup to which methylene chloride, 1.92 ml (30 mmoles), was added. The n.m.r. spectrum of the solution showed no significant amount of ethylene acetoxyiodide; nearly all of the ethylene diiodide was still present.

About 10 ml of methylene chloride was added to the reaction solution; after 4 days in the dark at 25°, the solution was evaporated to a syrup, methylene chloride, 1.92 ml (30 mmoles), added and the n.m.r. of the solution taken. More than 90% of the ethylene diiodide was found to have undergone reaction and 50-70% of it had been transformed to ethylene acetoxyiodide; this was shown by the intensities of the singlet at τ 6.32 and of the triplet centered at τ 5.70 relative to the intensities of the signals for methylene chloride and tetra-n-butylammonium ion. In addition, a singlet at τ 5.78 indicated the presence of about 10% ethylene diacetate.

Carbon tetrachloride was added and a black precipitate removed by filtration; the filtrate was evaporated and the residual syrup dissolved in methylene chloride, 0.32 ml (5.0 mmoles); in the n.m.r. spectrum

of the solution, the relative intensities of the signals for ethylene acetoxyiodide and methylene chloride indicated the presence of about 60% as much ethylene acetoxyiodide as methylene chloride. In addition there was present about 5% ethylene diiodide and about 10% of the compound giving rise to the signal at τ 5.78, probably ethylene diacetate.

Reaction of Ethylene Diiodide with Tetra-n-butylammonium Biacetate in the Presence of Cyclohexene

Ethylene diiodide, 1.409 g (5.0 mmoles), was added to a solution of tetra-n-butylammonium biacetate, 0.906 g (2.5 mmoles), and cyclohexene, 0.25 ml (2.5 mmoles), in 3 ml of methylene chloride; the solution rapidly became brown. After one hour, the n.m.r. spectrum of the solution was taken. The singlet at τ -4.9 for the acidic hydrogen of the biacetate and the band at τ 6.70 for the eight methylenic hydrogens geminal to nitrogen in the tetra-n-butylammonium ion had relative intensities 1:8, respectively. However, the sharp singlet at τ 6.30 for ethylene diiodide and the signal at τ -4.9 for the acidic hydrogen of the biacetate had relative intensities of 5:1, respectively; hence, about 35% of the diiodide had reacted. By the same technique, it was found that about 55% of the ethylene diiodide had reacted after 4 hours, about 70% after 24 hours, and about 90% after 4 days.

In the above n.m.r. spectra, it was noted that as the reaction progressed the signal due to the acidic proton of acetic acid in the complex

of acetic acid and tetra-n-butylammonium acetate moved steadily up-field. In solution in chloroform the acidic hydrogen of the biacetate had been noted to give rise to a signal at τ -6.7; in the above reaction, after one hour, the signal was found at τ -4.9, after 24 hours, at τ -1.3, and after 4 days at τ -0.2.

The solution was evaporated, the residue extracted with carbon tetrachloride, and the extract concentrated to a syrup by evaporation. The n.m.r. spectrum of the syrup (Fig. 30) showed the characteristic spectra of cyclohexene acetoxyiodide and ethylene acetoxyiodide, superimposed. Considerable ethylene diiodide was still present, as well, but there was no evidence of any acidic hydrogen. The relative intensities of the multiplet centered at τ 5.2 for cyclohexene acetoxyiodide, of the multiplets centered at τ 5.85 for cyclohexene acetoxyiodide and ethylene acetoxyiodide (two overlapping multiplets), of the singlet for ethylene diiodide at τ 6.30, and of the triplet centered at τ 6.67 for ethylene acetoxyiodide indicated a molar ratio of 1:1:4 for ethylene diiodide, ethylene acetoxyiodide, and cyclohexene acetoxyiodide, respectively.

Reaction of Ethylene Diiodide with Silver Acetate in the Presence of Cyclohexene

Silver acetate, 1.9 g (11 mmoles), and cyclohexene, 1.5 ml (15 mmoles), in 80 ml of acetic acid, were added to a solution of ethylene

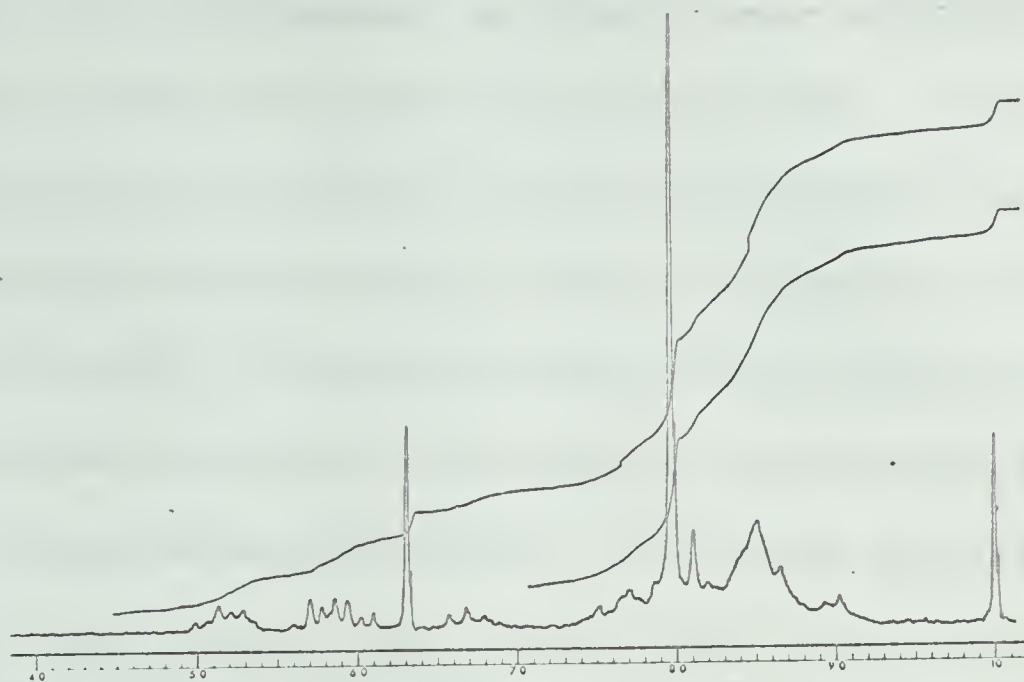


FIG. 30. N.m.r. spectrum (60 Mc.p.s.) of products of reaction of ethylene diiodide, tetra-*n*-butylammonium biacetate, and cyclohexene: corresponding to a 1 : 1 : 4 mixture of ethylene diiodide, ethylene acetoxyiodide, and cyclohexene trans-acetoxyiodide, respectively.

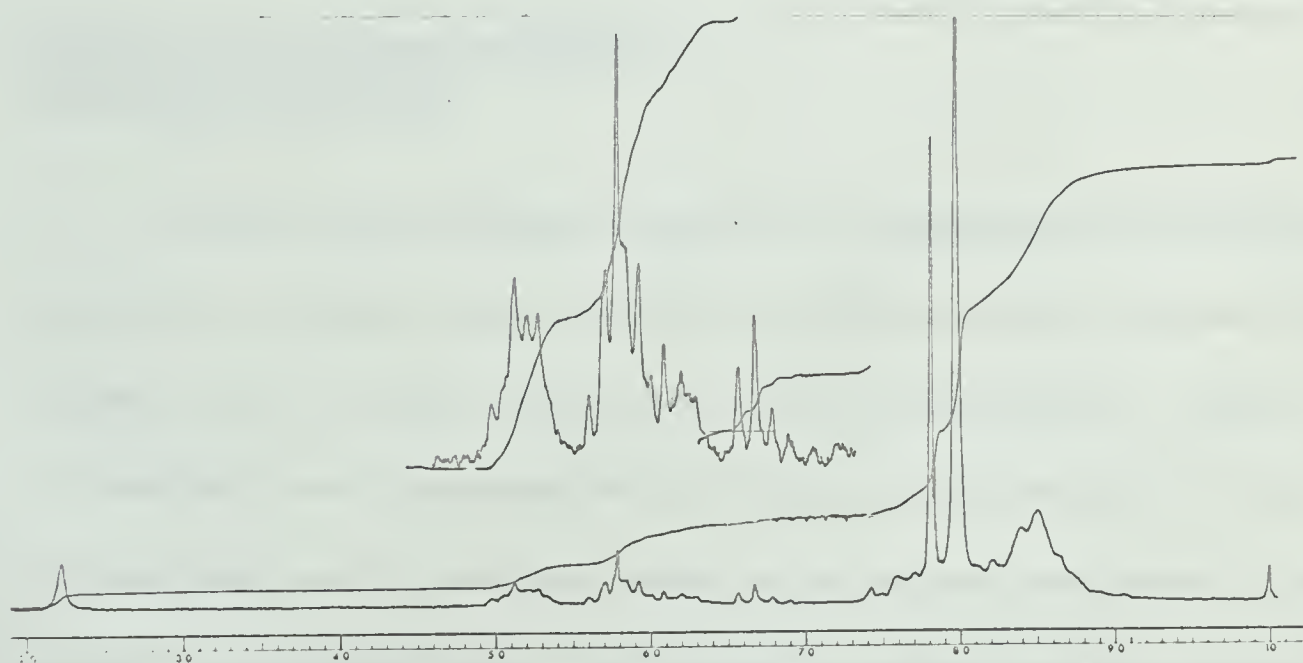


FIG. 31. N.m.r. spectrum (60 Mc.p.s.) of products of reaction of ethylene diiodide, silver acetate, and cyclohexene: corresponding to a 5 : 1 molar ratio of cyclohexene trans-acetoxyiodide to ethylene acetoxyiodide.

diiodide, 2.82 g (10 mmoles), in 10 ml of acetic anhydride and 10 ml of acetic acid and the mixture stirred for one day. At less than 50° , the mixture was evaporated, the residue extracted with carbon tetrachloride, and the extract concentrated to a syrup by evaporation. The n.m.r. spectrum of the syrup (Fig. 31) showed the characteristic spectra of cyclohexene acetoxiodide and ethylene acetoxiodide, superimposed, similar to the n.m.r. spectrum described above; the multiplet centered about τ 5.2 for cyclohexene acetoxiodide and the triplet centered about τ 6.67 for ethylene acetoxiodide had relative intensities about 5:2, respectively, indicating a molar ratio of 5:1 for cyclohexene acetoxiodide and ethylene acetoxiodide, respectively.

Reaction of Cyclohexene Diiodide with Sodium Methoxide

About 4 ml of methanol (dried over magnesium and distilled) was added to freshly scaled sodium, 1.0 g (40 mmoles), and the mixture refluxed to give, upon cooling, white sodium methoxide. Iodine, 5.0 g (20 mmoles), was dissolved, with cooling, in cyclohexene, 2.0 ml (20 mmoles), and the solution added to the sodium methoxide, contained in a dry ice-acetone bath. On thawing, a violent reaction ensued; hence, the mixture was re-cooled and then allowed to warm slowly until the violent reaction had subsided. The pale yellow heterogeneous mixture was refluxed for 15 minutes and allowed to cool, giving two liquid layers

and a white solid. Analysis by g.l.c. and n.m.r. spectroscopy of the upper layer showed it to consist mainly (about 95%) of cyclohexene, methanol being the chief minor component. In the same way, analysis of the lower layer showed it to consist mainly of methanol, cyclohexene, and a third component which was very volatile and appeared to be responsible for a sharp signal in the n.m.r. spectrum at τ 1.8 in the region expected for formaldehyde.

Reaction of Cyclohexene Diiodide with Ethyl Mercaptide Ion

In the following experiment, in order to obtain appreciable quantities of 1,2-bis(ethylthio)cyclohexane, it was found necessary to remove methanol and ethyl mercaptan as described.

Freshly scaled sodium, 4.6 g (200 mmoles), was added to 30 ml of dry methanol and the mixture refluxed until most of the sodium was dissolved; ethyl mercaptan, 20 ml (250 mmoles), was added and the mixture heated to obtain solution. Under reduced pressure, methanol and excess ethyl mercaptan were distilled off and the residual, pale yellow, cloudy solution cooled in a dry ice-acetone bath. Cyclohexene, 10 ml (100 mmoles), was cooled and iodine, 25 g (100 mmoles), added to it; this solution, containing cyclohexene diiodide, cyclohexene, and iodine, was added to the cold sodium mercaptide and the mixture allowed to warm to 25°. The mixture separated into two layers and a white solid settled out;

by g.l.c. analysis, the lower layer was shown to consist largely of methanol and ethyl mercaptan and the upper layer of ethyl mercaptan, cyclohexene, ethyl disulfide, and a fourth component, which had a retention time greater than any of the other components (relative ratio of last three compounds, 1:2:1, respectively)

The upper layer was separated, and 10 ml of water and 10 ml of diethyl ether added to it; the mixture was shaken, and the ethereal layer separated, dried, and evaporated; distillation under reduced pressure removed the lower boiling components and, as shown by g.l.c., the brown residual liquid consisted only of the fourth component mentioned above. This material was distilled at about 45° and a pressure of less than 1 mm. The n.m.r. spectrum (Fig. 24) of the collected material was taken at 100 Mc.p.s.. This showed a band centered at τ 7.23, a quartet centered at τ 7.45, a band at τ 7.7-8.0, a band at τ 8.2-8.65, and a triplet centered at τ 8.75 with relative integrated intensities of 2:4:2:6:6, respectively as required for 1,2-bis(ethylthio)cyclohexane. (The splittings in the quartet and triplet were all 7.5 c.p.s.).

Anal. Calcd. for $C_{10}H_{20}S_2$: C, 58.76; H, 9.86. Found:
C, 58.86; H, 9.74.

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1. The first part of the paper is devoted to the study of the

properties of the function $f(x)$ defined by the equation

$$f(x) = \frac{1}{2} (f(x-1) + f(x+1)).$$

It is shown that the function $f(x)$ is a linear function of x .

2. In the second part of the paper, we consider the function

$$g(x) = \frac{1}{2} (g(x-1) + g(x+1)).$$

It is shown that the function $g(x)$ is a linear function of x .

3. In the third part of the paper, we consider the function

$h(x)$ defined by the equation $h(x) = \frac{1}{2} (h(x-1) + h(x+1))$.

$$h(x) = \frac{1}{2} (h(x-1) + h(x+1)).$$

It is shown that the function $h(x)$ is a linear function of x .

$$h(x) = \frac{1}{2} (h(x-1) + h(x+1)).$$

4. In the fourth part of the paper, we consider the function

$k(x)$ defined by the equation $k(x) = \frac{1}{2} (k(x-1) + k(x+1))$.

It is shown that the function $k(x)$ is a linear function of x .

5. In the fifth part of the paper, we consider the function

$$l(x) = \frac{1}{2} (l(x-1) + l(x+1)).$$

It is shown that the function $l(x)$ is a linear function of x .

6. In the sixth part of the paper, we consider the function

$$m(x) = \frac{1}{2} (m(x-1) + m(x+1)).$$

It is shown that the function $m(x)$ is a linear function of x .

$$m(x) = \frac{1}{2} (m(x-1) + m(x+1)).$$

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